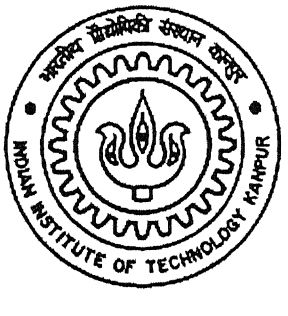
# PARAMETER ESTIMATION AND SIMULATION OF AROMATIC RECOVERY PROCESS USING LIQUID-LIQUID EXTRACTION AND EXTRACTIVE DISTILLATION

*A Thesis submitted*
In Partial Fulfillment of the Requirements
for the Degree of

**Master of Technology**

*by*

**Ranjan Kumar Sahoo**




*to the*

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
**August 2005**

# CERTIFICATE

It is certified that the work contained in this thesis entitled "**Parameter Estimation and Simulation of Aromatic Recovery Process using Liquid-Liquid Extraction and Extractive Distillation**" by Mr. Ranjan Kumar Sahoo has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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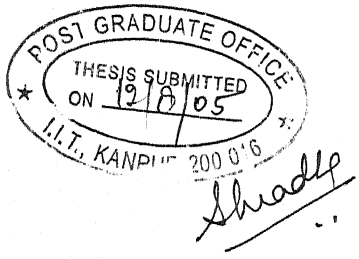

*Dedicated to.....*

*All those who raced against time,*
*but lost*

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Finally, I am indebted to my parents who have brought me up and encouraged me all the way.

Ranjan Kumar Sahoo

# Abstract

*Genetic Algorithm* (GA) has been applied to estimate binary interaction parameters for multicomponent liquid-liquid systems. However, these parameters are mutually interdependent through the ***closure equation/s***. For a $c$ component system there are $0.5\times c(c-3)+1$ closure equations. The binary interaction parameters have been estimated using GA, ***with and without closure equations*** for 53 ternary, 9 quaternary, and 3 quinary ***aromatic extraction systems***. Parameters that satisfy the closure equations gives approximately 12 percent better root mean square deviations (*rmsds*) than those that do not satisfy the closure equations. Invariably, GA gives approximately 42 percent better *rmsds* for NRTL and approximately 30 percent better *rmsds* for UNIQUAC than reported in the literature. GA has also been applied to 63 ternary and 2 quaternary ***hydrogen bonding systems***. For these systems GA gives approximately 55 percent better *rmsds* for NRTL and approximately 47 percent better *rmsds* for UNIQUAC than literature.

Complete ***aromatic recovery flowsheet*** has been simulated using ***liquid-liquid extraction*** and ***extractive distillation***. ***Aspen Plus 10.2***, a sequential modular simulation software package has been used to simulate the process flowsheet. To make the simulation realistic, ***murphree efficiencies*** calculated from ***ChemSep***, a simulator based on non-equilibrium model, have been used as input in Aspen Plus. Simulation using extraction has also been carried out with several ***mixed solvents*** (sulfolane+co-solvent). Performance of these alternatives has been compared in terms of ***performance index*** (PI). Mixed solvents with triethylene glycol and tetraethylene glycol as co-solvent gives better performance than dimethyl sulfoxide, n-methyl-2-pyrrolidone and n-methyl formamide. PI for extractive distillation is approximately three times better than extraction.

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# Chapter 1

# INTRODUCTION

## 1.1 Aromatic Recovery

Aromatic hydrocarbons such as benzene, toluene and xylenes (BTX) have wide applications and are considered essential in the modern organochemical industry. These are key petrochemical raw materials and their importance and versatility seems to increase with time. Benzene is the basic raw material for production of variety of chemicals like phenol, cyclohexane, anthraquinone, DDT, detergent alkylate, maleicanhydride and aniline. The other important uses of benzene include nylon, benzene hexachloride, 2,4-D bisphenol, dichlorobenzene, pentachlorophenol and aspirin. Toluene once thought of largely as the basis for TNT, is now finding expanding use as a solvent and as a chemical intermediate in the production of diisocynates, benzyl chloride, methyl styrene, saccharin and terphthalic acid etc. Toluene is also used as a blending stock for gasoline. Xylenes also have many uses. Oxidation of various xylenes to phthalic, isophthalic and terphthalic acids is typical of new and growing uses of aromatics. The other uses of aromatics are dehydrogenation of ethyl benzene to produce styrene monomer.

The major source of BTX aromatics is straight run or hydrogenated pyrolysis gasoline and catalytic reformates. These sources, apart from aromatics, contain large amount of other families (Paraffins, Isoparaffins, Olefins, Naphthenes, and Aromatics). Recovery and purification of the aromatic hydrocarbons from this complex mixture is therefore an important commercial process. It is impossible to obtain high purity of aromatics by classical distillation due to overlapping boiling ranges of feed components. Many homogeneous binary azeotropes exist between aliphatic and aromatic hydrocarbons. Aromatics can be purified using selective solvents that have a differential attraction to the aromatic ringed compounds. This can be done using liquid-liquid extraction (LLX) or by extractive distillation (ED). Equilibrium with the solvent in the liquid phase always has some impurities, which must be removed by other means, usually extractive stripping and water washing. LLX requires four major unit operations, a fairly

complicated process control, and is subject to solvent contamination by lighter hydrocarbons. The design calls for the removal of co-extracted light impurities in the stripper. In reality, the solvent builds up both light and heavy hydrocarbons and non-aromatic impurities in a substantial recycle. Feeds rich in naphthenes or olefins can further exacerbate the effect, increasing energy consumption significantly. The working principle of extractive distillation is the alteration of the relative volatility of components in the presence of a highly selective solvent, Conventional wisdom says that ED can only work with single carbon systems. This is true for many of the ED processes in use today. However, with the proper solvent choice and extractive distillation design, it is possible to cleanly separate BTX from a wide boiling range of feed components [1]. This technology has been commercially applied and proven in continuous operation since 2000. BTX recovery via extractive distillation is accomplished in two distillation towers. The first is an extractive distillation column, where the separation of the feed components occurs; and the second is a solvent recovery column, where the solvent is separated from the desired product. The extractive distillation column cleanly removes the non-aromatics from the aromatics and removes the aromatics and solvent from the raffinate in a single operation. Therefore, this design requires fewer pieces of equipment and a much lower capital cost than LLX system.

The economics of solvent extraction process largely depends on the choice of solvent. The solvents that are currently in use for aromatic extraction either have good selectivity for aromatics with simultaneously low solvent capacity or vice-versa. It is, therefore, imperative to search for new solvents as well as to evaluate the performance of existing solvents. The important parameters for the evaluation of solvent performance include solvent selectivity, solvent capacity, and solvent loss. Selectivity signifies the relative separation of two components. The solvent capacity signifies the amount of solvent for required separation. And the last parameter represents the solvent loss in the raffinate phase. These three parameters are defined in terms of activity coefficients of the components in both the raffinate and the extract phases. The accurate determination of liquid phase activity coefficients is usually obtained using the thermodynamic models – NRTL, UNIQUAC, or UNIFAC. These models require proper binary interaction

parameters, which represent the liquid-liquid equilibria for highly non-ideal liquid mixtures. Further, the design of equipment for solvent extraction requires accurate liquid-liquid equilibria data, which are either determined experimentally or predicted theoretically. Theoretical prediction again requires the liquid phase activity coefficients which are calculated from one of the thermodynamic models mentioned earlier. This in turn again requires the binary interaction parameters. Apart from the application in evaluating the performance of solvents and the design of extraction and extractive distillation unit the binary interaction parameters are also required for molecular design of new solvents. Availability of these parameters is also a compulsion for simulation. Therefore the availability of binary interaction parameters that can predict liquid-liquid equilibria accurately is of paramount importance. These parameters are yet not entirely available for very large component systems encountered in aromatic extraction. Process simulators like ASPEN PLUS are likely to produce drastic errors if used without accurate knowledge of these parameters. One can solve this problem by estimating the binary interaction parameters separately and specify them in ASPEN PLUS as user input instead of using the default parameters.

These binary interaction parameters are generally estimated using experimental liquid-liquid equilibrium data by optimizing a suitable objective function. In case no experimental liquid-liquid equilibria data for systems of concern are available, the infinite dilution activity coefficients can be used for parameter estimation, although at the cost of accuracy [2]. The optimization problem can be either the least square objective function minimization or likelihood function maximization. In both cases the objective function is nonlinear and nonconvex in terms of optimization variables; this possesses several local minima/maxima/saddle points within the specified bounds of the variables. Therefore, it is necessary to apply a technique that results in the global optimization of the variables. Evolutionary algorithms like genetic algorithm (GA) and simulated annealing (SA) can be used for the optimization. Further the binary interaction parameters are not all independent; in fact they are related through closure equation/s. It is therefore required to have such parameters which satisfy the closure equation/s.

## 1.2 Objective of the Thesis

Keeping in view the above considerations this thesis has been aimed at the following objectives:

- To generate the model dependent parameters of the models appropriate for aromatic extraction systems that can be used to predict multicomponent liquid-liquid equilibria.
- To simulate the aromatic recovery process using liquid-liquid extraction and extractive distillation.

## 1.3 Thesis Organization

The thesis is organized as follows

Chapter 2 presents the estimation of binary interaction parameters based on NRTL and UNIQUAC activity coefficient model for liquid-liquid extraction systems. A genetic algorithm, which is a structured search-based optimization method, has been used to minimize the highly nonlinear objective function encountered in liquid-liquid extraction.

Chapter 3 presents the estimation of binary interaction parameters with closure equation/s.

Chapter 4 presents the simulation and validation of complete aromatic recovery process using liquid-liquid extraction, with sulfolane as solvent.

Chapter 5 presents the comparative study of mixed solvents with sulfolane, on aromatic recovery process using liquid-liquid extraction.

Chapter 6 presents the simulation of complete aromatic recovery process using extractive distillation, with sulfolane as solvent.

Chapter 7 presents the recommendation for future work.

## References


[1] J. C. Gentry, S. Kumar, "Aromatic Design – The Future is Now!", 27th Annual *PETROCHEMICAL REVIEW*, Houston, Texas, March 2002.

[2] M. Mukhopadhyay, A. S. Pathak, "L-L-E data for aromatics extraction calculations using a modified UNIFAC model", *Industrial & Engineering Chemistry Process Design and Development* **25** (1986) 733.

# Chapter 2

# ESTIMATION OF BINARY INTERACTION PARAMETERS WITHOUT CLOSURE EQUATION/S

## 2.1 Introduction

Aromatics such as benzene, toluene, and xylene are considered essential in the chemical industry because they are the source of many organic chemicals. These aromatics are present in naphtha. High purity aromatics are difficult to be separated using ordinary distillation operation, since they form several binary azeotropes with nonaromatics. Extraction is therefore a better choice to separate the aromatics from naphtha, as they are preferentially soluble in a variety of solvents.

To predict the separation, it is necessary to know the liquid-liquid equilibrium (LLE) data for a particular system. Various activity coefficient models such as Non-Random Two Liquid (NRTL) and Universal Quasi Chemical (UNIQUAC) can be used to predict the LLE. Each of these models requires proper binary interaction parameters that can represent LLE for highly non-ideal liquid mixtures usually encountered in aromatic extraction. These parameters are usually estimated from the known experimental LLE data via optimization of a suitable objective function. The optimization problem can be either the least square objective function minimization or likelihood function maximization. In both cases the objective function is nonlinear and nonconvex in terms of optimization variables; this possesses several local minima/maxima/saddle points within the specified bounds of the variables. Therefore, it is necessary to apply a technique that results in the global optimization of the variables. Several such techniques are reported in literature, like Interval methods [1-2], Branch and Bound methods [3-6]. Despite the strong theoretical basis for these methods, the gradient evaluations and rounding off errors during computations give results that are definitely not globally optimal. Evolutionary algorithms like genetic algorithm (GA) [7, 8] and simulated annealing (SA) [8] have been rarely used for the optimization of LLE processes.

The binary interaction parameters for NRTL and UNIQUAC models are dependent on each other following a linear relationship called closure equation/s [9]. For a ternary triplet *i-j-k* the binary interaction parameters are related as [10],

$$(\tau_{jk} - \tau_{kj}) = (\tau_{ik} - \tau_{ki}) - (\tau_{ij} - \tau_{ji}) \quad (2.1)$$

The number of closure equations is one for ternary, three for quaternary and six for quinary systems [9]. However, in this chapter, the binary interaction parameters based on NRTL and UNIQUAC model have been estimated using GA without closure equation/s. The results thus obtained are compared with those reported in the literature.

## 2.2 Theory and Calculation

### 2.2.1 Genetic Algorithm (GA)

GA was first proposed by Holland [11, 12] and has been widely used in the recently. It is a method that searches for the global optima of an objective function through the use of simulated evolution; the survival of the fittest strategy. Unlike most of the optimization methods, GA does not require any initial guess but only the upper and lower bounds of the variables – in our case the interaction parameters. GA explores all regions of the solution space and exponentially exploits promising areas through selection, crossover and mutation operations applied to interaction parameters in the population. Float genetic algorithm (FGA) is better than both binary genetic algorithm (BGA) and SA in terms of computational efficiency and solution quality [13]. FGA has been used for the estimation of interaction parameters [13]. Flow diagram for FGA is given in Figure 2.1. FGA starts with initial populations of fixed size. Interaction parameters in the initial populations are generated randomly. Normalized geometric ranking, a probabilistic selection method, is used for the selection of populations. This method selects populations for next generation based on their fitness to the objective function. This is the role played by the probability of selecting the best individual ($q$). Remainder populations are randomly generated. Size of the population remains same in each generation. In each generation, new populations are generated using genetic operators – crossover (arithmetic, heuristic, and simple) and mutation (boundary, multi-non-uniform, non-uniform, and uniform). Relationships for selection function and operators are given in Table A.1 of Appendix A. GA moves from generation to generation until a termination criterion is met. The most frequently used stopping criterion is a specified maximum number of generations ($G_{max}$) [7, 13]. Various input parameters used for selection function and operators are given in Table 2.1. Finally GA

gives best population of interaction parameters which is available at the top of the list as organized by the ranking method from final generation as the required solution.

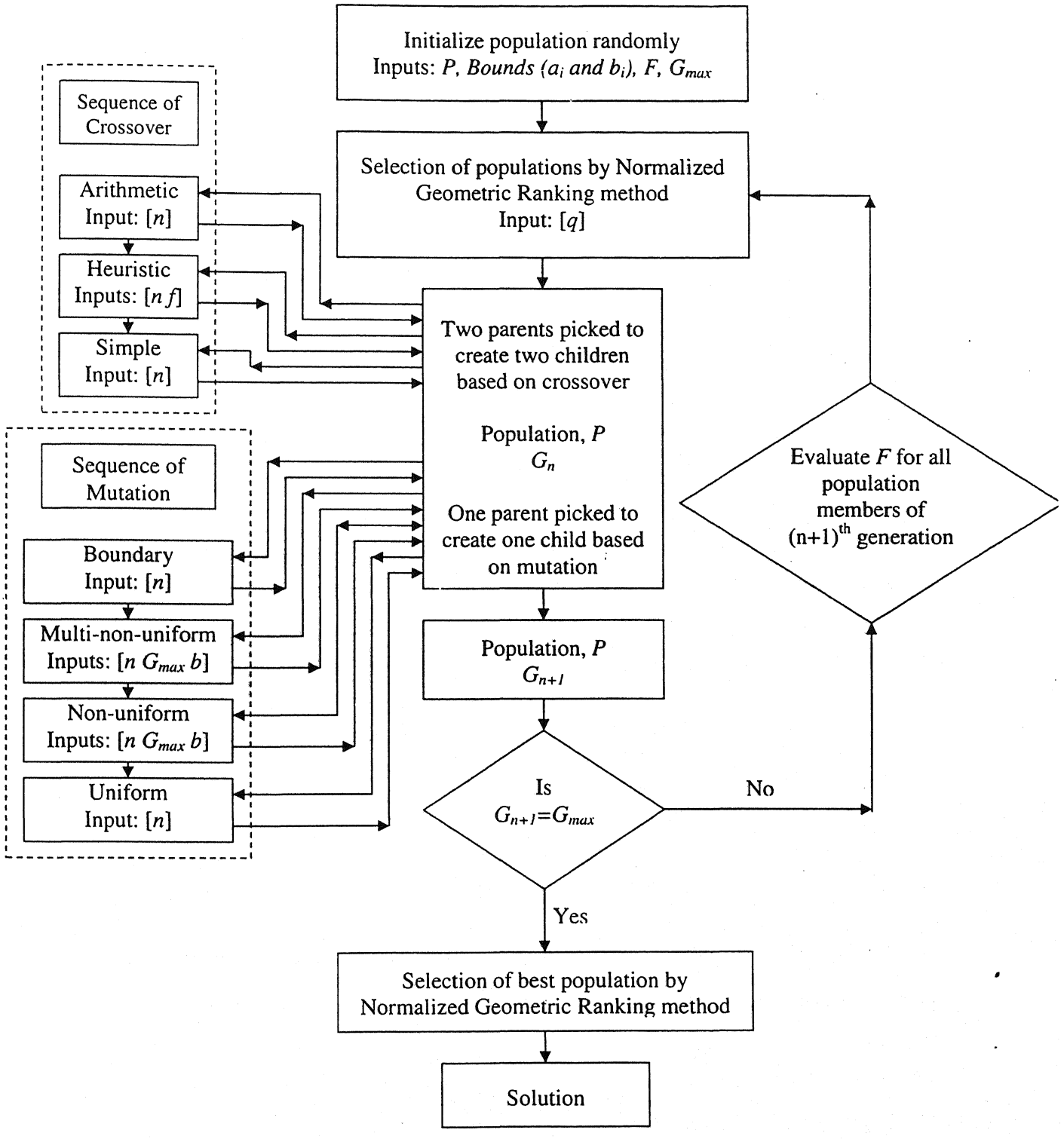


Figure 2.1 Flow diagram of float genetic algorithm (FGA)

Table 2.1 Values of the parameters used in GA Toolbox of matlab [13,14]

| Name | Parameters |
|---|---|
| Population size, $P$ | 100 |
| Maximum number of generations, $G_{max}$ | 200 |
| Normalized Geometric Selection, $q$ | [0.08] |
| Uniform Mutation | [4] |
| Non-Uniform Mutation | [4 $G_{max}$ 3] |
| Multi-Non-Uniform Mutation | [6 $G_{max}$ 3] |
| Boundary Mutation | [4] |
| Simple Crossover | [4] |
| Arithmetic Crossover | [4] |
| Heuristic Crossover | [2 3] |

All crossover and mutation operators have been used for our estimation. However, on could omit any of the crossover and/or mutation operators by setting 0 in the first entry of the corresponding input matrix.

**2.2.2 Activity Coefficient Models**

2.2.2.1 Non Random Two-Liquid (NRTL) model

The NRTL equation developed by Renon and Prausnitz [15, 16] represents an accepted extension of Wilson's concept. The NRTL equation is applicable to multicomponent vapor-liquid, liquid-liquid, and vapor-liquid-liquid systems. For a multicomponent system, the NRTL expression for the activity coefficient is [17, 18],

$$\ln \gamma_i = \frac{\sum_{j=1}^{c} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{c} G_{ki} x_k} + \sum_{j=1}^{c} \frac{x_j G_{ij}}{\sum_{k=1}^{c} G_{kj} x_k} \left( \tau_{ij} - \frac{\sum_{k=1}^{c} x_k \tau_{kj} G_{kj}}{\sum_{k=1}^{c} G_{kj} x_k} \right) \tag{2.2}$$

where $$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \tag{2.3}$$

The coefficients $\tau$ are given by $$\tau_{ji} = A_{ji} / T \tag{2.4}$$

where $A_{ji}$'s are the binary interaction parameters between the component $j$ and component $i$. In the above equations, $G_{ji} \neq G_{ij}$, $\tau_{ji} \neq \tau_{ij}$, $G_{ii} = G_{jj} = 1$, and $\tau_{ii} = \tau_{jj} = 0$. For ideal solutions, $\tau_{ji} = 0$.

The parameter $\alpha_{ji}$ characterizes the tendency of component $j$ and component $i$ to be distributed in a nonrandom fashion. When $\alpha_{ji}=0$, local mole fractions are equal to overall solution mole fractions. Generally $\alpha_{ji}$ is independent of temperature and depends on molecule properties. Values of $\alpha_{ji}$ usually lie between 0.2 and 0.47. Value of 0.2 for $\alpha_{ji}$ has been used in our work.

2.2.2.2 Universal Quasi-Chemical (UNIQUAC) model

In an attempt to place calculations of liquid-phase activity coefficients on a simple, yet more theoretical basis, Abrams and Prausnitz [19, 20] used statistical mechanics to derive an expression for excess free energy. Their model, called UNIQUAC, uses the local area fraction $\theta_i$ as the primary concentration variable instead of local mole fraction of NRTL model. The local area fraction is determined by representing a molecule by a set of bonded segments. Each molecule is characterized by two structural parameters that are determined relative to a standard segment taken as an equivalent sphere of a mer unit of a linear, infinite-length polymethylene molecule. The two structural parameters are the relative number of segments per molecule, $r_i$ (volume parameter), and the relative surface area of the molecule, $q_i$ (surface parameter).

For a multicomponent system, the UNIQUAC expression for the activity coefficient is [17, 18],

$$\ln\gamma_i=\ln\frac{\phi_i}{x_i}+\frac{z}{2}q_i\ln\frac{\theta_i}{\phi_i}+l_i-\frac{\phi_i}{x_i}\sum_{j=1}^{c}x_jl_j+q_i\left(1-\ln\sum_{j=1}^{c}\theta_j\tau_{ji}-\sum_{j=1}^{c}\frac{\theta_j\tau_{ij}}{\sum_{k=1}^{c}\theta_k\tau_{kj}}\right) \tag{2.5}$$

where

$$\phi_i=\frac{r_ix_i}{\sum_{j=1}^{c}r_jx_j}=\text{ segment fraction} \tag{2.6}$$

$$\theta_i=\frac{q_ix_i}{\sum_{j=1}^{c}q_jx_j}=\text{ area fraction} \tag{2.7}$$

$$l_i=\frac{z}{2}(r_i-q_i)+1-r_i \tag{2.8}$$

Where z = lattice coordination number set equal to 10, and

$$\tau_{ij} = \exp\left(-A_{ij}/T\right) \tag{2.9}$$

where $A_{ji}$'s are the binary interaction parameters between the component $j$ and component $i$. In the above equations, $\tau_{ii} = \tau_{jj} = 0$. Volume and surface ($r_i$ and $q_i$) parameters estimated from *Aspen Plus 10.0* have been used for our work.

### 2.2.3 Parameter Estimation Procedure

Binary interaction parameters are usually obtained from experimental LLE data by minimizing a suitable objective function. The most common objective function is the sum of the square of the error between the experimental and calculated composition of all the components over the entire set of tie-lines. As GA is only for maximization, for minimizing the errors between experimental and calculated mole fractions, the *objective function* can be defined as,

$$\text{Max.} \quad F = -\sum_{t=1}^{m}\sum_{l=1}^{II}\sum_{i=1}^{c} w_{it}^{l}\left(x_{it}^{l} - \hat{x}_{it}^{l}\right)^{2} \tag{2.10}$$

$$\text{w.r.t. } A_{ij} \qquad \text{where } i, j = 1, 2.....c \text{ and } j \neq i$$

This objective function, with unit weights i.e. $w_{it}^{l} = 1$, has been used in this work. The goodness of fit is usually measured by root mean square deviation (rmsd) defined as,

$$rmsd = \left(\frac{-F}{2mc}\right)^{1/2} \tag{2.11}$$

Modified Rachford Rice Algorithm [17] is used for the calculation of tie lines.

## 2.3 Results and Discussion

### 2.3.1 Aromatic extraction systems

Application of GA has been studied on 65 aromatic extraction systems; 53 ternary, 9 quaternary and 3 quinary systems as listed in Table 2.2.

Table 2.2 Ternary, quaternary and quinary aromatic extraction systems at different temperatures used for parameter estimation

| System No. | System Name | Temperature (°C) | Reference |
|---|---|---|---|
| | **Ternary Systems** | | |
| 1 | Pentane(1)-Benzene(2)-Sulfolane(3) | 17, 25, 50 | [21] |
| 2 | Pentane(1)-Toluene(2)-Sulfolane(3) | 17, 25, 50 | [21] |
| 3 | Hexane(1)-Benzene(2)-Sulfolane(3) | 25, 30, 50, 75, 100 | [22,23] |
| 4 | Hexane(1)-Toluene(2)-Sulfolane(3) | 25, 35, 50 | [24,25] |
| 5 | Hexane(1)-Xylene(2)-Sulfolane(3) | 25, 35, 50 | [24,25] |
| 6 | Heptane(1)-Benzene(2)-Sulfolane(3) | 25, 110 | [26,27] |
| 7 | Heptane(1)-Toluene(2)-Sulfolane(3) | 25, 30, 50, 75, 100 | [22,23] |
| 8 | Heptane(1)-Xylene(2)-Sulfolane(3) | 17, 25, 50 | [28] |
| 9 | Octane(1)-Benzene(2)-Sulfolane(3) | 25, 35, 45, 50, 75, 100 | [29,30] |
| 10 | Octane(1)-Toluene(2)-Sulfolane(3) | 25, 35, 45, 50, 75, 100 | [29,30] |
| 11 | Octane(1)-Xylene(2)-Sulfolane(3) | 25, 30, 35, 45, 50, 75, 100 | [23,29,30] |
| 12 | Cyclohexane(1)-Benzene(2)-Sulfolane(3) | 25, 50, 75, 100 | [22] |
| 13 | Cyclohexane(1)-Toluene(2)-Sulfolane(3) | 25 | [31] |
| 14 | Cyclohexane(1)-Xylene(2)-Sulfolane(3) | 35, 50 | [25] |
| 15 | 2-Methylpentane(1)-Toluene(2)-Sulfolane(3) | 25 | [31] |
| 16 | 1-Hexene(1)-Benzene(2)-Sulfolane(3) | 25, 50, 75, 100 | [22] |
| 17 | 1-Hexene(1)-Toluene(2)-Sulfolane(3) | 25 | [31] |
| 18 | 1-Heptene(1)-Benzene(2)-Sulfolane(3) | 25 | [32] |
| 19 | 1-Heptene(1)-Toluene(2)-Sulfolane(3) | 25 | [32] |
| 20 | Hexane(1)-Benzene(2)-Dimethyl Sulfoxide(3) | 10, 25, 50 | [33] |
| 21 | Heptane(1)-Benzene(2)-Dimethyl Sulfoxide(3) | 20.5 | [34] |
| 22 | Heptane(1)-Toluene(2)-Dimethyl Sulfoxide(3) | 25 | [34] |
| 23 | Cyclohexane(1)-Toluene(2)-Dimethyl Sulfoxide(3) | 20 | [34] |
| 24 | Heptane(1)-Ethylbenzene(2)-Ethylene Glycol(3) | 20, 30, 40, 50 | [35] |
| 25 | Heptane(1)-Benzene(2)-Diethylene Glycol(3) | 50 | [34] |
| 26 | Heptane(1)-Toluene(2)-Diethylene Glycol(3) | 25 | [34] |
| 27 | Hexane(1)-Benzene(2)-Triethylene Glycol(3) | 20 | [34] |
| 28 | Heptane(1)-Benzene(2)-Triethylene Glycol(3) | 20 | [34] |
| 29 | Heptane(1)-Toluene(2)-Triethylene Glycol(3) | 25 | [36] |
| 30 | Cyclohexane(1)-Benzene(2)-Triethylene Glycol(3) | 20 | [34] |
| 31 | Decane(1)-Benzene(2)-Tetraethylene Glycol(3) | 29, 45, 54.5 | [37] |
| 32 | Decane(1)-Ethylbenzene(2)-Tetraethylene Glycol(3) | 25.5, 39, 50 | [37] |
| | | | *(continued on next page)* |

| | | | |
|---|---|---|---|
| 33 | Heptane(1)-Benzene(2)-Thiodiglycol(3) | 50 | [26] |
| 34 | Heptane(1)-Toluene(2)-Thiodiglycol(3) | 50 | [26] |
| 35 | Hexane(1)-Benzene(2)-N-Methyl Pyrrolidone(3) | 25 | [38] |
| 36 | Heptane(1)-Benzene(2)-N-Methyl Pyrrolidone(3) | 25 | [34] |
| 37 | Heptane(1)-Toluene(2)-N-Methyl Pyrrolidone(3) | 15, 25, 40 | [39] |
| 38 | Hexane(1)-Benzene(2)-N-Methylformamide(3) | 20, 25 | [38,34] |
| 39 | Heptane(1)-Benzene(2)-N-Methylformamide(3) | 20 | [34] |
| 40 | Hexane(1)-Benzene(2)-Dimethylformamide(3) | 25 | [38] |
| 41 | Heptane(1)-Benzene(2)-Dimethylformamide(3) | 20 | [34] |
| 42 | Dodecane(1)-Benzene(2)-Dimethylformamide(3) | 20, 30, 40 | [35] |
| 43 | Dodecane(1)-Ethylbenzene(2)-Dimethylformamide(3) | 20, 30, 40, 50 | [35] |
| 44 | Heptane(1)-Ethylbenzene(2)-Ethylene Carbonate(3) | 40, 45, 50, 55, 60 | [40] |
| 45 | Heptane(1)-Toluene(2)-Propylene Carbonate(3) | 25 | [41] |
| 46 | Heptane(1)-Xylene(2)-Propylene Carbonate(3) | 25 | [41] |
| 47 | Heptane(1)-Toluene(2)-Benzyl Alcohol(3) | 25 | [36] |
| 48 | Heptane(1)-Toluene(2)-3-Methyl Sulfolane(3) | 25 | [26] |
| 49 | Heptane(1)-Toluene(2)-Mercaptoethanol(3) | 25 | [26] |
| 50 | Hexane(1)-Benzene(2)-Furfural(3) | 25 | [42] |
| 51 | Hexane(1)-Toluene(2)-Furfural(3) | 25 | [42] |
| 52 | Hexane(1)-Xylene(2)-Furfural(3) | 25 | [42] |
| 53 | Cyclohexane(1)-Benzene(2)-Furfural(3) | 25 | [34] |
| | **Quaternary Systems** | | |
| 54 | Hexane(1)-Benzene(2)-Xylene(3)-Sulfolane(4) | 25 | [24] |
| 55 | Heptane(1)-Benzene(2)-Toluene(3)-Sulfolane(4) | 25 | [43] |
| 56 | Octane(1)-Toluene(2)-Xylene(3)-Sulfolane(4) | 25 | [24] |
| 57 | Hexane(1)-Heptane(2)-Toluene(3)-Sulfolane(4) | 25 | [43] |
| 58 | Hexane(1)-Octane(2)-Benzene(3)-Sulfolane(4) | 25 | [24] |
| 59 | Heptane(1)-Octane(2)-Xylene(1)-Sulfolane(4) | 25 | [43] |
| 60 | Cyclohexane(1)-1-Heptene(2)-Benzene(3)-Sulfolane(4) | 25 | [32] |
| 61 | Cyclohexane(1)-1-Heptene(2)-Toluene(3)-Sulfolane(4) | 25 | [32] |
| 62 | Heptane(1)-Toluene(2)-Triethylene Glycol(3)-Benzyl Alcohol(4) | 25, 40 | [36] |
| | **Quinary Systems** | | |
| 63 | Hexane(1)-Heptane(2)-Toluene(3)-Xylene(4)-Sulfolane(5) | 25 | [43] |
| 64 | Hexane(1)-Octane(2)-Benzene(3)-Toluene(4)-Sulfolane(5) | 25 | [24] |
| 65 | Heptane(1)-Octane(2)-Benzene(3)-Xylene(4)-Sulfolane(5) | 25 | [43] |

UNIQUAC structural parameters as given in Table 2.3 have been estimated using *Aspen Plus 10.0*, a steady state simulator [44].

Table 2.3 UNIQUAC volume and area parameters for aromatic extraction systems [44]

| Component Name | $r_i$ | $q_i$ | Component Name | $r_i$ | $q_i$ |
|---|---|---|---|---|---|
| Pentane | 3.82531 | 3.316 | Dimethyl Sulfoxide | 2.82663 | 2.472 |
| Hexane | 4.49967 | 3.856 | Ethylene Glycol | 2.40870 | 2.248 |
| Heptane | 5.17403 | 4.396 | Diethylene Glycol | 4.00132 | 3.568 |
| Octane | 5.84838 | 4.936 | Triethylene Glycol | 5.59394 | 4.880 |
| Decane | 7.19842 | 6.016 | Tetraethylene Glycol | 7.18655 | 6.208 |
| Dodecane | 8.54318 | 7.096 | Thiodiglycol | 4.53527 | 3.848 |
| Cyclohexane | 4.04746 | 3.240 | N-Methyl Pyrrolidone | 3.98088 | 3.200 |
| 2-Methylpentane | 4.49901 | 3.852 | N-Methyl Formamide | 2.40277 | 2.192 |
| 1-Hexene | 4.26961 | 3.644 | N,N-Dimethyl Formamide | 3.08570 | 2.736 |
| 1-Heptene | 4.94397 | 4.184 | Ethylene Carbonate | 2.51945 | 1.972 |
| Benzene | 3.19051 | 2.400 | Propylene Carbonate | 2.97891 | 2.280 |
| Toluene | 3.92287 | 2.968 | Benzyl Alcohol | 4.22610 | 3.244 |
| Xylene | 4.65788 | 3.536 | 3-Methyl Sulfolane | 4.70929 | 3.736 |
| Ethylbenzene | 4.59723 | 3.520 | 2-Mercaptoethanol | 2.85498 | 2.544 |
| Sulfolane | 4.03560 | 3.200 | Furfural | 3.17205 | 2.500 |

The benchmarking system involves the predictions of LLE for cyclohexane (1)-xylene (2)-sulfolane (3) ternary system at 35 °C.

2.3.1.1 Lower and Upper Bounds, ($a_i$ and $b_i$)

The effect of the value of bounds on the interaction parameters and rmsd values for both NRTL and UNIQUAC model is given in Table 2.4. Minimum rmsd is observed at a bound of -1000 and +2000 for NRTL and -1000 and +1000 for UNIQUAC model. The lower values of these for both the model, estimate some of the interaction parameters at the edge of the boundary. Keeping this in mind we have chosen -1000 and +2000 for NRTL and -1000 and +1000 for UNIQUAC model as the lower and upper bounds for our estimation.

Table 2.4 Effect of bounds on binary interaction parameters and rmsd values for the system cyclohexane (1)-xylene (2)-sulfolane (3) at 35 °C

| Bounds | | Binary Interaction Parameters (K) | | | rmsd | Hitting Bound | |
|---|---|---|---|---|---|---|---|
| | | $A_{12}$ | $A_{13}$ | $A_{23}$ | | | |
| Lower | Upper | $A_{21}$ | $A_{31}$ | $A_{32}$ | | Lower | Upper |
| NRTL | | | | | | | |
| -200 | +200 | **-200.00** | **200.00** | **200.00** | 0.1171 | Yes | Yes |
| | | **-200.00** | **200.00** | **200.00** | | | |
| -500 | +500 | **-500.00** | **500.00** | **500.00** | 0.0285 | Yes | Yes |
| | | -357.19 | **500.00** | 107.94 | | | |
| -1000 | +1000 | -686.06 | **1000.00** | **1000.00** | 0.0062 | No | Yes |
| | | 973.89 | 539.14 | 42.06 | | | |
| -1000 | +1500 | -221.23 | **1500.00** | 806.99 | 0.0053 | No | Yes |
| | | 90.94 | 496.30 | 92.04 | | | |
| -1000 | +2000 | 652.78 | 1382.10 | 1028.10 | **0.0048** | No | No |
| | | -580.17 | 550.55 | 49.327 | | | |
| -1500 | +2500 | -283.10 | 1844.90 | 732.09 | 0.0052 | No | No |
| | | 178.21 | 500.89 | 120.88 | | | |
| -2000 | +3000 | -312.03 | 1147.20 | 1049.90 | 0.0058 | No | No |
| | | 122.05 | 502.93 | -2.92 | | | |
| UNIQUAC | | | | | | | |
| -200 | +200 | -105.67 | **200.00** | **200.00** | 0.0172 | No | Yes |
| | | 84.29 | **200.00** | 31.12 | | | |
| -500 | +500 | -20.93 | **500.00** | 229.16 | 0.0067 | No | Yes |
| | | 7.78 | 92.78 | 14.92 | | | |
| -1000 | +1000 | -233.41 | 662.70 | 269.03 | **0.0056** | No | No |
| | | 422.52 | 67.80 | 9.20 | | | |
| -1500 | +1500 | 237.05 | 356.13 | 910.79 | 0.0068 | No | No |
| | | -229.09 | 127.34 | -137.64 | | | |
| -2000 | +2000 | -355.88 | 668.98 | 562.32 | 0.0074 | No | No |
| | | 840.04 | 35.41 | -98.37 | | | |

### 2.3.1.2 Population size, *P*

Effect of population size on absolute objective function value for NRTL and UNIQUAC model is shown in Figure 2.2 and Figure 2.3 respectively. It is observed that, for both the model population size of 100 is sufficient to give good set of parameters. Therefore, population size of 100 has been chosen for both the model.

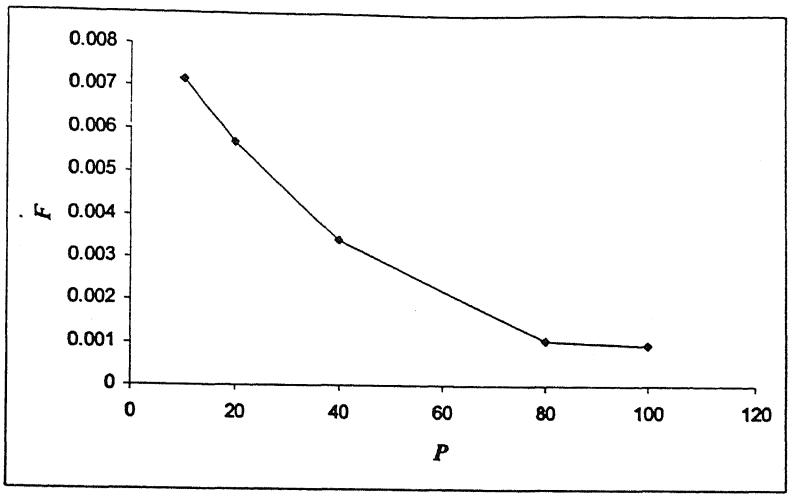


Figure 2.2 Effect of population size on absolute objective function value for NRTL model

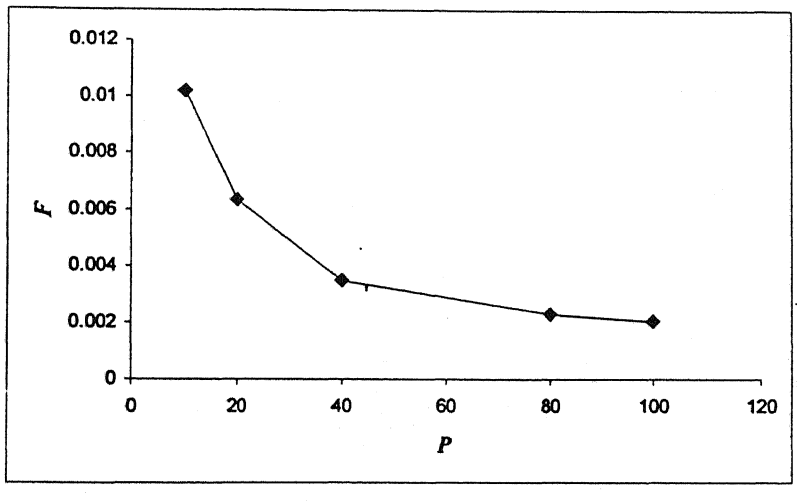


Figure 2.3 Effect of population size on absolute objective function value for UNIQUAC model

2.3.1.3 Maximum number of Generation, $G_{max}$

Variation of absolute objective function value against generation number for NRTL and UNIQUAC model is shown in Figure 2.4 and Figure2.5 respectively. It is observed that, for both the model 200$^{th}$ generation is sufficient to give a very good set of parameters; further generations only seem to improve marginally upon the solution obtained. Therefore, value of 200 for $G_{max}$ has been used for both the model.

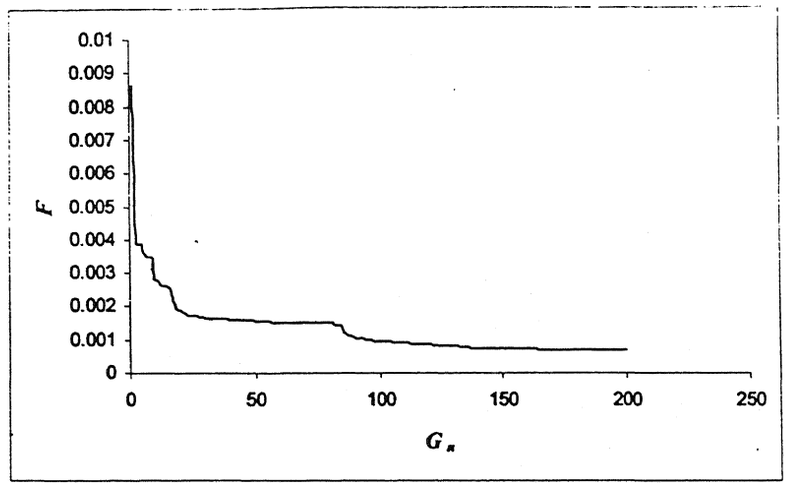


Figure 2.4 Absolute value of objective function versus generation number for NRTL model

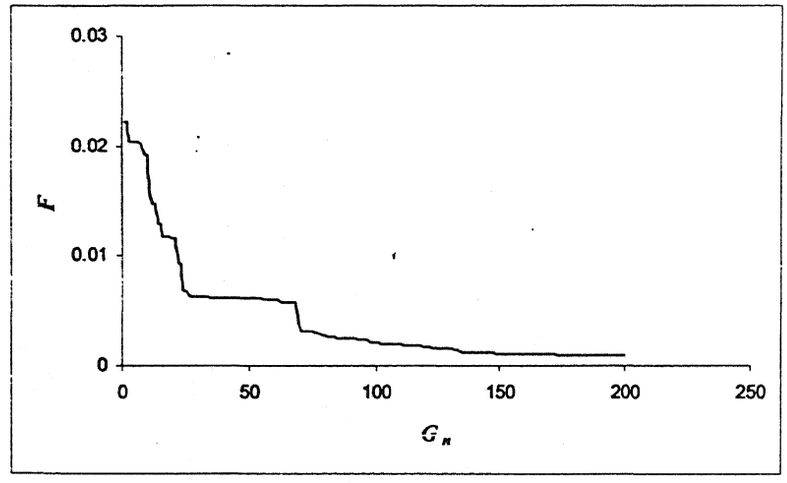


Figure 2.5 Absolute value of objective function versus generation number for UNIQUAC model

Comparison of tie-line compositions for NRTL and UNIQUAC model are given in Table 2.5 and Table 2.6 respectively. The rmsd value thus obtained is 0.005 and 0.006 compared to 0.010 and 0.011 in the literature, respectively for NRTL and UNIQUAC model.

Table 2.5 Comparison of tie-lines for cyclohexane (1)-xylene (2)- sulfolane (3) at 35 °C [25] using NRTL model

| Experimental | | | | | | Predicted | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| solvent rich phase | | | non-aromatic rich phase | | | solvent rich phase | | | non-aromatic rich phase | | |
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ | $\hat{x}_1$ | $\hat{x}_2$ | $\hat{x}_3$ | $\hat{x}_1$ | $\hat{x}_2$ | $\hat{x}_3$ |
| 0.0241 | 0.0394 | 0.9365 | 0.7230 | 0.2710 | 0.0060 | 0.0288 | 0.0397 | 0.9316 | 0.7201 | 0.2713 | 0.0086 |
| 0.0225 | 0.0568 | 0.9206 | 0.6456 | 0.3457 | 0.0087 | 0.0279 | 0.0553 | 0.9168 | 0.6414 | 0.3478 | 0.0108 |
| 0.0312 | 0.1050 | 0.8639 | 0.4303 | 0.5520 | 0.0178 | 0.0247 | 0.1133 | 0.8620 | 0.4372 | 0.5442 | 0.0185 |
| 0.0316 | 0.1694 | 0.8000 | 0.3154 | 0.6658 | 0.0188 | 0.0244 | 0.1626 | 0.8131 | 0.3162 | 0.6616 | 0.0222 |
| 0.0259 | 0.1018 | 0.8723 | 0.4540 | 0.5276 | 0.0185 | 0.0250 | 0.1042 | 0.8708 | 0.4559 | 0.5261 | 0.0180 |
| **rmsd [lit]=0.010** | | | | | | **rmsd=0.005** | | | | | |

Table 2.6 Comparison of tie-lines for cyclohexane (1)-xylene (2)- sulfolane (3) at 35 °C [25] using UNIQUAC model

| Experimental | | | | | | Predicted | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| solvent rich phase | | | non-aromatic rich phase | | | solvent rich phase | | | non-aromatic rich phase | | |
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ | $\hat{x}_1$ | $\hat{x}_2$ | $\hat{x}_3$ | $\hat{x}_1$ | $\hat{x}_2$ | $\hat{x}_3$ |
| 0.0241 | 0.0394 | 0.9365 | 0.7230 | 0.2710 | 0.0060 | 0.0276 | 0.0418 | 0.9305 | 0.7250 | 0.2704 | 0.0046 |
| 0.0225 | 0.0568 | 0.9206 | 0.6456 | 0.3457 | 0.0087 | 0.0266 | 0.0572 | 0.9162 | 0.6456 | 0.3472 | 0.0072 |
| 0.0312 | 0.1050 | 0.8639 | 0.4303 | 0.5520 | 0.0178 | 0.0238 | 0.1104 | 0.8658 | 0.4352 | 0.5440 | 0.0208 |
| 0.0316 | 0.1694 | 0.8000 | 0.3154 | 0.6658 | 0.0188 | 0.0237 | 0.1614 | 0.8149 | 0.3128 | 0.6558 | 0.0314 |
| 0.0259 | 0.1018 | 0.8723 | 0.4540 | 0.5276 | 0.0185 | 0.0240 | 0.1028 | 0.8732 | 0.4551 | 0.5257 | 0.0192 |
| **rmsd [lit]=0.011** | | | | | | **rmsd=0.006** | | | | | |

After benchmarking with the above system, GA has been applied and verified on other ternary, quaternary and quinary systems. The rmsd values obtained using GA have been compared with the rmsd values reported in literature in terms of percentage gain,

$$gain_{lit}^{ga} = \frac{rmsd_{lit} - rmsd_{ga}}{rmsd_{lit}} \times 100 \qquad (2.12)$$

The results of NRTL parameter estimation along with the corresponding percentage gain values for the ternary, quaternary and quinary systems are given in Table 2.7-2.9 respectively. It is seen that the rmsd values obtained using GA are less than those reported in the literature; approximately 37 percent better for ternary and 26 percent better for both quaternary and quinary systems. This clearly means that parameters obtained using GA will predict the multicomponent aromatic extraction LLE for NRTL model more accurately than those reported in the literature.

Table 2.7 NRTL (α=0.2) binary interaction parameters without closure equation for ternary aromatic extraction systems at different temperatures

| System No. | Temp. (°C) | Binary Interaction Parameters (K) | | | | | | rmsd | rmsd [lit] | $gain_{lit}^{ga}$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $A_{12}$ | $A_{21}$ | $A_{13}$ | $A_{31}$ | $A_{23}$ | $A_{32}$ | | | |
| 1 | 17 | 456.25 | 1022.80 | 921.28 | 671.21 | 696.20 | 638.55 | 0.0064 | n.a. | n.a. |
| | 25 | 83.31 | 53.45 | 1381.70 | 961.14 | 574.24 | -203.80 | 0.0037 | n.a. | n.a. |
| | 50 | -120.03 | 1045.00 | 1010.50 | 713.04 | 729.20 | 101.57 | 0.0047 | n.a. | n.a. |
| 2 | 17 | 383.88 | -259.62 | 1696.70 | 733.14 | 534.54 | -56.76 | 0.0051 | n.a. | n.a. |
| | 25 | 543.26 | 1466.40 | 1719.40 | 547.63 | 434.38 | 1024.60 | 0.0041 | n.a. | n.a. |
| | 50 | 208.99 | -118.07 | 1350.60 | 507.36 | 810.83 | -170.13 | 0.0067 | n.a. | n.a. |
| 3 | 25 | -541.55 | 537.64 | 1494.40 | 656.85 | 472.60 | -351.07 | 0.005 | n.a. | n.a. |
| | 30 | 877.91 | 467.41 | 1125.50 | 646.25 | 378.52 | 979.40 | 0.007 | n.a. | n.a. |
| | 50 | -93.71 | -76.59 | 1190.90 | 793.17 | 876.38 | -484.31 | 0.004 | n.a. | n.a. |
| | 75 | -68.38 | -127.15 | 1208.80 | 667.42 | 785.05 | -407.42 | 0.006 | n.a. | n.a. |
| | 100 | 336.19 | -224.50 | 1635.30 | 734.97 | 412.86 | -49.38 | 0.004 | n.a. | n.a. |
| 4 | 25 | -446.11 | 872.28 | 1036.30 | 530.36 | 806.27 | -198.20 | 0.006 | 0.005 | -20.00 |
| | 35 | -116.83 | 22.63 | 1489.40 | 656.59 | 934.37 | -73.03 | 0.009 | 0.016 | 43.75 |
| | 50[a] | 28.17 | 3274.70 | 3173.50 | 869.69 | 762.29 | 566.98 | 0.005 | 0.015 | 66.67 |
| 5 | 25 | 220.86 | 1646.80 | 1613.80 | 647.78 | 370.84 | 824.81 | 0.005 | 0.008 | 37.50 |
| | 35 | -105.71 | -137.64 | 1480.90 | 625.47 | 1098.40 | 123.16 | 0.004 | 0.016 | 75.00 |
| | 50 | -676.47 | 565.81 | 1384.20 | 706.72 | 1087.80 | 52.65 | 0.002 | 0.010 | 80.00 |
| 6 | 25 | 145.79 | 915.00 | 1256.50 | 699.26 | 654.81 | 345.11 | 0.0042 | n.a. | n.a. |
| | 110 | 337.64 | 982.14 | 931.86 | 748.11 | 537.94 | 705.19 | 0.004 | n.a. | n.a. |
| 7 | 25 | 537.47 | -488.82 | 1388.10 | 1357.30 | 10750 | -302.33 | 0.005 | n.a. | n.a. |
| | 30 | 44.76 | 915.48 | 816.51 | 914.38 | -296.61 | 1234.40 | 0.002 | n.a. | n.a. |
| | 50 | 272.97 | -263.32 | 1470.40 | 912.71 | 615.44 | -95.82 | 0.002 | n.a. | n.a. |
| | 75 | 686.47 | -662.95 | 1464.60 | 924.81 | 1019.10 | -321.48 | 0.004 | n.a. | n.a. |
| | 100 | -384.38 | 317.74 | 1326.60 | 677.39 | 340.21 | 21.49 | 0.003 | n.a. | n.a. |
| 8 | 17 | 855.25 | -580.18 | 1274.00 | 1306.30 | 949.90 | -132.91 | 0.013 | n.a. | n.a. |
| | 25 | -486.17 | 879.93 | 1758.80 | 778.21 | 447.20 | 184.19 | 0.005 | n.a. | n.a. |
| | 50 | -235.06 | 519.63 | 1592.10 | 794.64 | 322.26 | 315.13 | 0.006 | n.a. | n.a. |
| 9 | 25 | 1311.70 | 867.26 | 1022.00 | 883.59 | 855.47 | 1216.50 | 0.005 | 0.006 | 16.67 |
| | 35 | 267.81 | 1661.80 | 779.34 | 885.75 | 1248.80 | 350.50 | 0.006 | 0.009 | 33.33 |
| | 45 | 462.14 | 1125.10 | 1037.60 | 986.90 | 646.75 | 721.14 | 0.004 | 0.005 | 20.00 |
| | 50 | -104.80 | 1634.10 | 1082.30 | 779.20 | 1003.10 | 186.15 | 0.005 | 0.006 | 16.67 |
| | 75 | 577.11 | 1209.00 | 1205.30 | 878.30 | 637.75 | 916.39 | 0.003 | 0.003 | 0.00 |
| | 100 | 470.00 | 626.52 | 1512.40 | 1118.70 | 269.02 | 879.40 | 0.004 | 0.009 | 55.56 |
| 10 | 25 | -331.83 | 601.35 | 914.09 | 1010.20 | 718.49 | -48.24 | 0.002 | 0.002 | 0.00 |
| | 35 | -258.31 | 300.85 | 1060.60 | 1097.00 | 439.97 | 15.20 | 0.002 | 0.002 | 0.00 |
| | 45 | 663.27 | 1750.70 | 979.39 | 954.49 | 367.74 | 1231.50 | 0.002 | 0.003 | 33.33 |
| | 50 | 361.57 | 1557.60 | 1708.20 | 847.26 | 564.96 | 831.47 | 0.006 | 0.007 | 14.29 |
| | 75 | 174.36 | 1305.30 | 1470.60 | 927.84 | 455.25 | 769.58 | 0.003 | 0.005 | 40.00 |
| | 100 | -425.86 | 481.00 | 1295.30 | 903.08 | 712.38 | -108.57 | 0.003 | 0.004 | 25.00 |
| 11 | 25 | -257.91 | 7.20 | 794.27 | 1054.00 | 935.71 | -225.64 | 0.003 | 0.003 | 0.00 |

(*continued on next page*)

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 30 | 620.80 | -183.17 | 910.55 | 1121.40 | 339.60 | 145.99 | 0.003 | n.a. | n.a. |
| | 35 | 426.48 | 1455.40 | 1539.10 | 915.95 | 184.01 | 1200.80 | 0.002 | 0.003 | 33.33 |
| | 45 | -438.97 | 1198.60 | 872.64 | 819.66 | 601.85 | 128.24 | 0.004 | 0.003 | -33.33 |
| | 50 | -192.35 | 132.23 | 1208.50 | 1047.40 | 841.48 | -40.48 | 0.002 | 0.002 | 0.00 |
| | 75 | 437.81 | -415.58 | 1369.60 | 1220.30 | 937.89 | -146.06 | 0.004 | 0.003 | -33.33 |
| | 100 | 35.86 | 20.82 | 1271.70 | 1099.50 | 560.79 | 158.14 | 0.003 | 0.004 | 25.00 |
| 12 | 25 | -232.20 | 175.30 | 1471.30 | 463.15 | 447.11 | -241.87 | 0.004 | n.a. | n.a. |
| | 50 | 949.50 | 398.63 | 1530.00 | 438.72 | 236.62 | 1148.60 | 0.003 | n.a. | n.a. |
| | 75 | 1265.30 | 518.21 | 1354.20 | 388.48 | 248.51 | 1594.60 | 0.004 | n.a. | n.a. |
| | 100 | 568.14 | -234.82 | 1500.30 | 375.42 | -34.95 | 586.49 | 0.004 | n.a. | n.a. |
| 13 | 25 | 350.31 | -576.15 | 1286.50 | 856.96 | 986.43 | -414.56 | 0.008 | 0.010 | 20.00 |
| 14 | 35 | 652.78 | -580.17 | 1382.10 | 550.55 | 1028.10 | 49.33 | 0.005 | 0.010 | 50.00 |
| | 50 | -406.02 | 333.63 | 1430.20 | 403.17 | 799.62 | 67.88 | 0.006 | 0.011 | 45.46 |
| 15 | 25 | -10.62 | -235.08 | 1185.10 | 986.02 | 823.05 | -386.26 | 0.007 | 0.014 | 50.00 |
| 16 | 25 | 252.97 | 510.44 | 1274.30 | 468.95 | 299.77 | 546.14 | 0.003 | n.a. | n.a. |
| | 50 | 1326.50 | 292.79 | 1531.90 | 473.39 | 121.89 | 1496.50 | 0.004 | n.a. | n.a. |
| | 75 | -446.44 | 744.16 | 1204.40 | 405.69 | 297.82 | 32.93 | 0.004 | n.a. | n.a. |
| | 100 | 1280.80 | 424.47 | 1123.40 | 432.65 | 187.93 | 1574.10 | 0.004 | n.a. | n.a. |
| 17 | 25 | 1222.30 | 964.25 | 1700.30 | 735.54 | 144.28 | 1643.70 | 0.007 | 0.010 | 30.00 |
| 18 | 25 | 335.16 | -348.59 | 1288.20 | 632.34 | 439.42 | -122.97 | 0.005 | 0.007 | 28.57 |
| 19 | 25 | 744.26 | -569.41 | 1167.50 | 731.91 | 692.36 | -104.11 | 0.004 | 0.006 | 33.33 |
| 20 | 10 | 1054.80 | 1324.80 | 1469.80 | 626.29 | 587.88 | 1280.40 | 0.0048 | n.a. | n.a. |
| | 25 | 1134.90 | 1188.00 | 1148.50 | 578.42 | 728.41 | 1248.00 | 0.0063 | n.a. | n.a. |
| | 50 | -540.86 | 418.63 | 1016.50 | 677.40 | 332.08 | -306.52 | 0.0035 | n.a. | n.a. |
| 21 | 20.5 | 1131.20 | 1348.10 | 961.29 | 576.56 | 583.22 | 1299.20 | 0.0046 | n.a. | n.a. |
| 22 | 25 | 572.64 | 1281.20 | 1073.30 | 818.48 | 213.85 | 1209.60 | 0.0066 | n.a. | n.a. |
| 23 | 20 | 556.64 | 1654.00 | 1150.40 | 420.72 | 315.62 | 1145.50 | 0.0025 | n.a. | n.a. |
| 24 | 20 | 1576.10 | 178.20 | 737.53 | 1145.30 | 998.93 | 738.85 | 0.0047 | n.a. | n.a. |
| | 30 | 69.73 | 94.76 | 582.85 | 1273.70 | 949.72 | 697.54 | 0.0047 | n.a. | n.a. |
| | 40 | 88.82 | 362.60 | 468.37 | 1134.10 | 1329.20 | 747.43 | 0.0029 | n.a. | n.a. |
| | 50[b] | 2834.20 | 253.88 | 325.71 | 1241.00 | 2799.80 | 781.58 | 0.0088 | n.a. | n.a. |
| 25 | 50 | -214.24 | 436.93 | 1139.80 | 1523.60 | 954.36 | -54.37 | 0.0057 | n.a. | n.a. |
| 26 | 25 | -472.13 | 783.64 | 1887.90 | 718.83 | 1336.10 | 115.03 | 0.0020 | n.a. | n.a. |
| 27 | 20 | -267.01 | 316.95 | 1395.50 | 654.23 | 1649.40 | -329.52 | 0.0039 | n.a. | n.a. |
| 28 | 20 | -501.55 | 813.06 | 1803.30 | 666.13 | 1428.10 | -288.54 | 0.0036 | n.a. | n.a. |
| 19 | 25 | -106.76 | 331.68 | 1667.10 | 731.62 | 1408.80 | -106.21 | 0.0017 | n.a. | n.a. |
| 30 | 20 | -510.14 | 1019.60 | 1778.10 | 380.87 | 1201.60 | -194.22 | 0.0060 | n.a. | n.a. |
| 31 | 29 | 88.43 | 1293.90 | 163.38 | 1699.60 | 404.94 | 640.21 | 0.0063 | n.a. | n.a. |
| | 45 | 115.67 | 1463.40 | 290.76 | 1413.70 | 389.38 | 734.96 | 0.0101 | n.a. | n.a. |
| | 54.5 | -242.81 | 422.36 | 640.64 | 1744.00 | 270.92 | 178.81 | 0.0033 | n.a. | n.a. |
| 32 | 25.5 | 34.47 | 1564.70 | 442.10 | 1689.00 | 723.14 | 590.74 | 0.0040 | n.a. | n.a. |
| | 39 | -713.14 | 402.29 | 965.90 | 1059.90 | 298.84 | 280.47 | 0.0071 | n.a. | n.a. |
| | 50 | -386.58 | 1045.40 | 930.03 | 1444.70 | 132.96 | 673.73 | 0.0083 | n.a. | n.a. |
| 33 | 50 | 355.89 | -120.76 | 1934.20 | 961.84 | 1198.80 | 85.85 | 0.0032 | n.a. | n.a. |
| | | | | | | | | | | |

*(continued on next page)*

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 34 | 50 | -190.63 | 234.80 | 1701.80 | 962.08 | 1292.50 | 181.91 | 0.0020 | n.a. | n.a. |
| 35 | 25 | 1619.20 | 467.15 | 548.86 | 317.76 | 584.56 | 1490.60 | 0.0029 | 0.0077 | 62.34 |
| 36 | 25 | 975.74 | -299.75 | 503.54 | 485.15 | -211.99 | 723.64 | 0.0021 | n.a. | n.a. |
| 37 | 15 | 714.87 | -187.70 | 542.68 | 432.14 | 752.61 | -109.60 | 0.004 | 0.004 | 0.00 |
| | 25 | 1124.10 | -164.57 | 470.13 | 433.38 | 555.05 | 339.72 | 0.002 | 0.004 | 50.00 |
| | 40 | 699.15 | 730.52 | 379.06 | 400.05 | 646.88 | 656.87 | 0.002 | 0.014 | 85.71 |
| 38 | 20 | -422.00 | 226.74 | 1104.90 | 435.76 | 1482.60 | -428.29 | 0.0059 | n.a. | n.a. |
| | 25 | 130.24 | -286.90 | 1295.40 | 476.59 | 1010.70 | -284.06 | 0.0026 | 0.0096 | 72.92 |
| 39 | 20 | 626.46 | -593.53 | 1786.50 | 802.52 | 1191.20 | -281.04 | 0.0019 | n.a. | n.a. |
| 40 | 25 | -554.39 | 1453.70 | 1311.40 | 389.10 | 829.71 | -38.61 | 0.0036 | 0.007 | 48.57 |
| 41 | 20 | 531.63 | 124.83 | 571.12 | 509.84 | 44.70 | 646.23 | 0.0012 | n.a. | n.a. |
| 42 | 20 | 783.96 | 1361.20 | 485.63 | 938.94 | 758.25 | 947.95 | 0.0032 | n.a. | n.a. |
| | 30 | 205.17 | -347.18 | 567.88 | 1082.70 | -484.93 | 508.77 | 0.0044 | n.a. | n.a. |
| | 40 | 1351.60 | -397.84 | 445.65 | 1019.70 | -645.99 | 1879.80 | 0.0084 | n.a. | n.a. |
| 43 | 20 | 374.97 | 1550.00 | 442.51 | 816.00 | 274.02 | 1703.50 | 0.0077 | n.a. | n.a. |
| | 30 | 592.04 | 527.44 | 803.31 | 825.31 | -120.73 | 1640.40 | 0.0070 | n.a. | n.a. |
| | 40 | 111.70 | 74.00 | 317.07 | 1185.90 | 1143.10 | -161.03 | 0.0080 | n.a. | n.a. |
| | 50 | 498.82 | 349.10 | 295.07 | 1104.90 | 638.17 | 309.25 | 0.0057 | n.a. | n.a. |
| 44 | 40 | -55.18 | -223.46 | 1559.30 | 1582.60 | 819.27 | 159.02 | 0.0022 | n.a. | n.a. |
| | 45 | -140.75 | 216.91 | 1190.60 | 1561.90 | 947.58 | 305.13 | 0.0010 | n.a. | n.a. |
| | 50 | 539.84 | -395.27 | 1326.90 | 1583.50 | 799.42 | 273.31 | 0.0008 | n.a. | n.a. |
| | 55 | -166.32 | -753.17 | 1564.60 | 1827.40 | 649.29 | -49.24 | 0.0044 | n.a. | n.a. |
| | 60 | -609.80 | 405.76 | 1335.10 | 1739.20 | 671.10 | 239.48 | 0.0013 | n.a. | n.a. |
| 45 | 25 | -116.91 | 1415.90 | 1382.60 | 540.75 | 632.88 | 375.54 | 0.0027 | n.a. | n.a. |
| 46 | 25 | -311.78 | 1438.90 | 1868.70 | 624.65 | 686.04 | 276.40 | 0.0022 | n.a. | n.a. |
| 47 | 25 | -338.15 | -375.15 | 527.68 | 343.86 | -46.16 | -511.07 | 0.0026 | n.a. | n.a. |
| 48 | 25 | 1059.90 | 1845.20 | 921.07 | 409.48 | 777.95 | 1213.00 | 0.0050 | n.a. | n.a. |
| 49 | 25 | -321.49 | 798.45 | 755.75 | 637.61 | 595.92 | 203.04 | 0.0037 | n.a. | n.a. |
| 50 | 25 | 1242.20 | 570.05 | 671.59 | 412.15 | 390.42 | 1581.10 | 0.003 | 0.002 | -50.00 |
| 51 | 25 | 674.90 | 898.86 | 544.61 | 497.69 | 257.92 | 1203.40 | 0.004 | 0.003 | -33.33 |
| 52 | 25 | 559.16 | -701.96 | 673.37 | 465.84 | 1584.40 | -405.18 | 0.002 | 0.002 | 0.00 |
| 53 | 25 | -309.24 | 290.41 | 601.88 | 305.36 | 1027.60 | -521.27 | 0.004 | n.a. | n.a. |
| **average rmsd** | | | | | | | | **0.0043** | **0.0068** | **36.77** |

[a] bounds -1000 and 3500; [b] bounds -1000 and 3000; n.a.: not available/not applicable

Table 2.8 NRTL (α=0.2) binary interaction parameters without closure equations for quaternary aromatic extraction systems at 25°C (r=40°C)

| System No. | Binary Interaction Parameters (K) | | | | | | rmsd | rmsd [*lit*] | $gain_{lit}^{ga}$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| | $A_{12}$ | $A_{13}$ | $A_{14}$ | $A_{23}$ | $A_{24}$ | $A_{34}$ | | | |
| | $A_{21}$ | $A_{31}$ | $A_{41}$ | $A_{32}$ | $A_{42}$ | $A_{43}$ | | | |
| 54 | -651.35 | -614.30 | 921.68 | -745.34 | 592.84 | 1361.20 | 0.006 | 0.007 | 14.29 |
| | 540.59 | 179.77 | 650.79 | 292.85 | -500.19 | -475.80 | | | |
| 55 | 3.73 | 659.27 | 958.93 | -638.35 | 1039.70 | 363.83 | 0.005 | 0.006 | 16.67 |
| | 971.46 | 149.80 | 882.79 | 1816.70 | -43.56 | 503.99 | | | |

(*continued on next page*)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 56 | 1315.40 | -305.55 | 1873.30 | 1517.00 | 177.70 | 309.47 | 0.005 | 0.007 | 28.57 |
| | 919.65 | 1144.30 | 1121.30 | 1451.00 | 1599.60 | 510.94 | | | |
| 57 | 414.97 | 918.21 | 1063.70 | -497.92 | 862.68 | 895.99 | 0.004 | 0.005 | 20.00 |
| | -120.76 | -353.32 | 1154.10 | 1788.00 | 631.12 | -89.05 | | | |
| 58 | 745.31 | -572.39 | 662.50 | -295.25 | 809.98 | 1077.10 | 0.006 | 0.010 | 40.00 |
| | 254.36 | 1055.60 | 818.68 | 235.79 | 1919.20 | -564.37 | | | |
| 59 | 1814.90 | 761.98 | 1345.40 | 229.37 | 1743.80 | 445.87 | 0.004 | 0.007 | 42.86 |
| | -371.12 | 102.58 | 1041.70 | -93.96 | 1028.00 | 215.15 | | | |
| 60 | 1278.00 | 101.150 | 1063.60 | 982.27 | 1855.20 | 193.83 | 0.004 | 0.004 | 0.00 |
| | 1169.50 | -294.43 | 967.74 | 1309.20 | 936.21 | 332.42 | | | |
| 61 | 401.61 | -238.53 | 650.37 | 1425.10 | 1237.40 | 691.68 | 0.006 | 0.009 | 33.33 |
| | 624.89 | 905.69 | 748.66 | -524.34 | 1118.60 | -42.96 | | | |
| 62 | -596.17 | 1264.60 | 567.06 | 1157.80 | 648.32 | -411.23 | 0.006 | n.a. | n.a. |
| | 209.67 | 1162.00 | 342.39 | 951.68 | -647.38 | 1349.00 | | | |
| 62[r] | -525.90 | 1734.50 | 560.74 | 1861.10 | -502.70 | 1391.40 | 0.005 | n.a. | n.a. |
| | 480.25 | 365.13 | 583.97 | 154.31 | 1061.30 | 278.64 | | | |
| **average rmsd** | | | | | | | **0.0051** | **0.0069** | **26.09** |

n.a.: not available/not applicable

Table 2.9 NRTL (α=0.2) binary interaction parameters without closure equations for quinary aromatic extraction systems at 25 °C

| System No. | Binary Interaction Parameters (K) | | | | | rmsd | rmsd [*lit*] | $gain_{lit}^{ga}$ (%) |
|---|---|---|---|---|---|---|---|---|
| | $A_{12}$ | $A_{21}$ | $A_{31}$ | $A_{41}$ | $A_{51}$ | | | |
| | $A_{13}$ | $A_{23}$ | $A_{32}$ | $A_{42}$ | $A_{52}$ | | | |
| | $A_{14}$ | $A_{24}$ | $A_{34}$ | $A_{43}$ | $A_{53}$ | | | |
| | $A_{15}$ | $A_{25}$ | $A_{35}$ | $A_{45}$ | $A_{54}$ | | | |
| 63 | 406.83 | -749.91 | -345.52 | 277.34 | 525.76 | 0.007 | 0.009 | 22.22 |
| | 1162.20 | 1131.70 | -498.16 | -501.77 | 1009.70 | | | |
| | -257.87 | 842.35 | 280.87 | 77.73 | 91.65 | | | |
| | 1089.80 | 850.84 | 910.38 | 1381.60 | -164.50 | | | |
| 64 | -407.20 | 1143.10 | 440.56 | 403.01 | 988.47 | 0.005 | 0.004 | -25.00 |
| | -234.05 | -247.28 | 871.27 | 287.48 | 1076.00 | | | |
| | 733.82 | 1226.10 | 1687.60 | -250.42 | -188.67 | | | |
| | 1549.50 | 1514.80 | 701.46 | 55.49 | 1219.70 | | | |
| 65 | -352.44 | -913.25 | 129.32 | 416.13 | 364.81 | 0.005 | 0.010 | 50.00 |
| | -567.84 | -562.94 | 554.58 | -62.22 | 545.43 | | | |
| | -315.21 | 302.24 | -456.37 | 975.84 | -379.63 | | | |
| | 1214.10 | 1044.50 | 776.28 | 527.00 | 394.42 | | | |
| **average rmsd** | | | | | | **0.0057** | **0.0077** | **25.97** |

Table 2.10 UNIQUAC binary interaction parameters without closure equation for ternary aromatic extraction systems at different temperatures

| System No. | Temp. (°C) | Binary Interaction Parameters (K) | | | | | | rmsd | rmsd [lit] | $gain_{lit}^{ga}$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $A_{12}$ | $A_{21}$ | $A_{13}$ | $A_{31}$ | $A_{23}$ | $A_{32}$ | | | |
| 1 | 17 | 412.47 | 389.67 | 249.81 | 173.43 | 248.82 | 562.69 | 0.0093 | n.a. | n.a. |
| | 25 | 299.39 | 294.02 | 305.22 | 174.75 | 169.73 | 456.52 | 0.0059 | n.a. | n.a. |
| | 50 | 563.12 | 161.62 | 359.38 | 191.34 | 88.30 | 729.03 | 0.0054 | n.a. | n.a. |
| 2 | 17 | 255.62 | 14.34 | 939.21 | 115.72 | -30.60 | 360.30 | 0.0070 | n.a. | n.a. |
| | 25 | 232.74 | -169.78 | 513.61 | 113.05 | 179.43 | -23.70 | 0.0035 | n.a. | n.a. |
| | 50 | 174.62 | -121.38 | 457.64 | 78.69 | 255.78 | -58.57 | 0.0068 | n.a. | n.a. |
| 3 | 25 | 185.16 | 203.53 | 425.12 | 64.56 | 180.62 | 261.62 | 0.006 | n.a. | n.a. |
| | 30 | 302.37 | 148.87 | 402.28 | 58.89 | 164.53 | 350.75 | 0.009 | n.a. | n.a. |
| | 50 | -664.14 | -34.40 | 955.72 | 47.84 | -71.47 | -544.40 | 0.005 | n.a. | n.a. |
| | 75 | -956.98 | 5.92 | 543.36 | 34.64 | 33.54 | -845.98 | 0.008 | n.a. | n.a. |
| | 100 | 194.92 | 273.54 | 449.27 | 57.12 | 140.70 | 401.97 | 0.006 | n.a. | n.a. |
| 4 | 25 | 376.29 | -254.21 | 503.51 | 154.16 | 691.71 | -226.01 | 0.005 | n.a. | n.a. |
| | 35 | -241.63 | 784.76 | 394.88 | 113.61 | 349.78 | 11.88 | 0.010 | 0.020 | 50.00 |
| | 50 | 87.77 | -217.21 | 506.97 | 81.15 | 856.47 | -188.20 | 0.005 | 0.011 | 54.55 |
| 5 | 25 | -196.24 | 329.87 | 274.75 | 100.28 | 399.50 | -108.52 | 0.007 | n.a. | n.a. |
| | 35 | 27.70 | -112.07 | 361.03 | 89.01 | 674.28 | -93.00 | 0.004 | 0.012 | 66.67 |
| | 50 | -441.27 | 580.28 | 499.93 | 94.90 | 392.71 | -100.13 | 0.004 | 0.018 | 77.78 |
| 6 | 25 | 332.70 | -157.97 | 654.05 | 116.48 | -60.78 | 238.29 | 0.0051 | n.a. | n.a. |
| | 110 | 650.76 | -265.12 | 465.70 | 88.51 | -91.75 | 347.40 | 0.008 | n.a. | n.a. |
| 7 | 25 | -284.26 | 530.78 | 352.56 | 62.75 | 356.88 | -124.44 | 0.009 | n.a. | n.a. |
| | 30 | -94.27 | 594.14 | 314.51 | 115.03 | -112.89 | 466.29 | 0.002 | n.a. | n.a. |
| | 50 | -203.89 | 465.75 | 442.53 | 61.64 | 205.13 | 22.00 | 0.004 | n.a. | n.a. |
| | 75 | 576.39 | -355.54 | 641.47 | 44.21 | 666.25 | -230.20 | 0.003 | n.a. | n.a. |
| | 100 | 230.35 | -21.09 | 713.01 | 6.48 | -41.85 | 376.82 | 0.004 | n.a. | n.a. |
| 8 | 17 | -178.17 | 535.50 | 348.11 | 125.42 | 188.92 | 56.41 | 0.009 | n.a. | n.a. |
| | 25 | 13.77 | 177.77 | 917.27 | 209.17 | 8.476 | 257.08 | 0.008 | n.a. | n.a. |
| | 50 | -49.37 | 383.36 | 549.13 | 133.37 | 74.41 | 239.34 | 0.008 | n.a. | n.a. |
| 9 | 25 | -621.01 | 12.31 | 348.05 | 95.00 | 772.47 | -861.32 | 0.004 | 0.004 | 0.00 |
| | 35 | 194.43 | 102.68 | 216.97 | 304.17 | 240.21 | 135.73 | 0.007 | 0.009 | 22.22 |
| | 45 | 164.24 | 632.31 | 350.44 | 69.71 | 711.75 | 217.04 | 0.006 | 0.006 | 0.00 |
| | 50 | -951.27 | -16.47 | 423.40 | 271.85 | -62.82 | -825.94 | 0.008 | 0.005 | -60.00 |
| | 75 | 93.39 | 76.95 | 500.85 | 46.84 | 137.19 | 129.14 | 0.003 | 0.004 | 25.00 |
| | 100 | 438.43 | 155.46 | 485.26 | 52.25 | 131.67 | 566.27 | 0.006 | 0.008 | 25.00 |
| 10 | 25 | -897.10 | 823.54 | 369.84 | 79.79 | 324.74 | -675.93 | 0.007 | 0.002 | -250.00 |
| | 35 | -42.88 | 190.77 | 216.70 | 335.54 | 134.96 | 103.49 | 0.005 | 0.003 | -66.67 |
| | 45 | -15.92 | -28.36 | 152.26 | 544.02 | 366.45 | -125.70 | 0.008 | 0.003 | -166.67 |
| | 50 | 913.09 | -414.59 | 793.50 | 192.49 | 864.51 | -264.26 | 0.007 | 0.007 | 0.00 |
| | 75 | 143.72 | 196.32 | 654.91 | 50.28 | 94.87 | 323.72 | 0.004 | 0.005 | 20.00 |
| | 100 | 79.63 | 758.91 | 490.89 | 54.93 | 278.26 | 369.28 | 0.003 | 0.005 | 40.00 |
| 11 | 25 | 383.47 | -228.34 | 438.13 | 504.51 | -39.74 | 202.25 | 0.007 | 0.004 | -75.00 |

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| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 30 | 230.54 | 101.22 | 147.10 | 406.52 | 203.13 | 205.09 | 0.009 | n.a. | n.a. |
| | 35 | -847.59 | 751.23 | 475.37 | 61.40 | 178.64 | -535.67 | 0.008 | 0.004 | -100.00 |
| | 45 | 336.22 | 468.06 | 462.55 | 55.56 | 155.68 | 561.39 | 0.004 | 0.005 | 20.00 |
| | 50 | -293.35 | 669.26 | 374.99 | 81.69 | 709.46 | -142.61 | 0.006 | 0.006 | 0.00 |
| | 75 | 272.59 | 527.99 | 400.27 | 260.62 | 81.04 | 648.09 | 0.008 | 0.004 | -100.00 |
| | 100 | 147.38 | -114.96 | 530.16 | 67.62 | 185.25 | 20.70 | 0.003 | 0.003 | 0.00 |
| 12 | 25 | -663.21 | 215.16 | 382.56 | 84.86 | 114.67 | -539.76 | 0.006 | n.a. | n.a. |
| | 50 | 552.94 | 100.53 | 519.99 | 50.47 | 30.27 | 675.56 | 0.005 | n.a. | n.a. |
| | 75 | 408.01 | 356.73 | 426.26 | 51.58 | 140.37 | 651.55 | 0.007 | n.a. | n.a. |
| | 100 | 608.74 | 24.05 | 614.31 | 8.64 | -82.61 | 923.88 | 0.004 | n.a. | n.a. |
| 13 | 25 | 241.88 | -234.28 | 466.67 | 157.48 | 313.26 | -142.11 | 0.008 | n.a. | n.a. |
| 14 | 35 | -233.41 | 422.52 | 662.70 | 67.80 | 269.03 | 9.20 | 0.006 | 0.011 | 45.45 |
| | 50 | -287.95 | 846.14 | 381.20 | 94.80 | 405.77 | -21.90 | 0.006 | 0.016 | 62.50 |
| 15 | 25 | -98.98 | 772.45 | 282.85 | 112.93 | 395.13 | 50.34 | 0.009 | n.a. | n.a. |
| 16 | 25 | -212.97 | -5.83 | 443.76 | 55.71 | -14.03 | -104.80 | 0.005 | n.a. | n.a. |
| | 50 | -695.20 | 220.91 | 356.92 | 49.71 | 162.43 | -575.39 | 0.007 | n.a. | n.a. |
| | 75 | 431.75 | -281.76 | 495.82 | 21.38 | 473.47 | -196.85 | 0.004 | n.a. | n.a. |
| | 100 | 565.15 | 314.56 | 389.22 | 27.96 | 151.16 | 853.04 | 0.005 | n.a. | n.a. |
| 17 | 25 | 128.35 | 179.32 | 391.73 | 162.04 | -6.05 | 381.73 | 0.007 | n.a. | n.a. |
| 18 | 25 | -477.21 | 334.52 | 401.90 | 25.02 | 127.79 | -276.24 | 0.009 | n.a. | n.a. |
| 19 | 25 | 410.40 | 95.52 | 457.60 | 99.84 | -58.26 | 651.37 | 0.009 | n.a. | n.a. |
| 20 | 10 | -935.82 | 834.51 | 574.56 | 45.96 | 713.18 | -857.56 | 0.0094 | n.a. | n.a. |
| | 25 | -219.82 | 294.97 | 912.64 | 39.83 | 122.71 | -74.27 | 0.0038 | n.a. | n.a. |
| | 50 | 454.12 | 72.82 | 526.45 | 64.57 | 146.93 | 455.64 | 0.0030 | n.a. | n.a. |
| 21 | 20.5 | 159.25 | 602.36 | 455.87 | 19.98 | 643.37 | 239.17 | 0.0078 | n.a. | n.a. |
| 22 | 25 | 71.25 | 502.62 | 539.10 | 66.52 | 237.22 | 273.92 | 0.0049 | n.a. | n.a. |
| 23 | 20 | -64.12 | 98.90 | 567.15 | 49.06 | 127.86 | 36.63 | 0.0039 | n.a. | n.a. |
| 24 | 20 | -78.55 | 363.69 | 509.77 | 100.13 | 574.02 | 116.77 | 0.0051 | n.a. | n.a. |
| | 30 | 174.81 | -161.98 | 408.57 | 157.39 | 561.63 | 73.87 | 0.0047 | n.a. | n.a. |
| | 40 | -297.99 | 796.27 | 370.60 | 129.65 | 978.93 | 70.91 | 0.0036 | n.a. | n.a. |
| | 50[a] | 1930.80 | -155.34 | 297.64 | 184.34 | 1546.50 | 60.71 | 0.0098 | n.a. | n.a. |
| 25 | 50 | -45.37 | 83.60 | 159.76 | 341.14 | 294.33 | -23.86 | 0.0074 | n.a. | n.a. |
| 26 | 25 | 625.80 | -290.31 | 594.61 | 50.64 | 725.67 | -86.69 | 0.0020 | n.a. | n.a. |
| 27 | 20 | -191.13 | 925.92 | 176.31 | 179.25 | 257.45 | 39.55 | 0.0074 | n.a. | n.a. |
| 28 | 20 | 364.14 | -207.26 | 391.16 | 100.55 | 312.70 | -71.17 | 0.0031 | n.a. | n.a. |
| 29 | 25 | 238.15 | -99.42 | 767.47 | 47.36 | 7.87 | 175.00 | 0.0063 | n.a. | n.a. |
| 30 | 20 | 92.04 | -5.55 | 379.75 | 94.38 | 28.29 | 157.97 | 0.0078 | n.a. | n.a. |
| 31 | 29 | 92.22 | 81.47 | -89.85 | 358.72 | -70.79 | 347.97 | 0.0087 | n.a. | n.a. |
| | 45 | -118.38 | 126.48 | -118.01 | 488.12 | 518.48 | -153.88 | 0.0102 | n.a. | n.a. |
| | 54.5 | 526.94 | -331.17 | 73.97 | 353.02 | 171.53 | -100.25 | 0.0063 | n.a. | n.a. |
| 32 | 25.5 | -63.35 | 328.40 | -108.21 | 607.41 | 620.45 | -13.89 | 0.0061 | n.a. | n.a. |
| | 39 | -611.54 | 725.49 | 146.45 | 109.79 | 53.06 | -103.04 | 0.0088 | n.a. | n.a. |
| | 50 | 516.48 | -286.35 | 69.28 | 234.79 | 16.99 | 135.14 | 0.0108 | n.a. | n.a. |
| 33 | 50 | 692.63 | -258.14 | 594.04 | 83.39 | 289.33 | 66.20 | 0.0038 | n.a. | n.a. |
| | | | | | | | | | | |

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| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 34 | 50 | 292.35 | -196.82 | 618.26 | 81.85 | 285.49 | 57.43 | 0.0022 | n.a. | n.a. |
| 35 | 25 | 147.90 | 80.96 | 232.59 | 13.57 | 220.52 | 51.27 | 0.0035 | 0.0060 | 41.67 |
| 36 | 25 | -742.16 | 256.83 | 226.43 | -2.72 | 358.77 | -838.30 | 0.0069 | n.a. | n.a. |
| 37 | 15 | -369.97 | 796.59 | 254.38 | 12.17 | 4.0653 | -107.56 | 0.003 | 0.004 | 25.00 |
| | 25 | -348.60 | -139.97 | 221.56 | 27.46 | -209.41 | -292.48 | 0.004 | 0.004 | 0.00 |
| | 40 | -651.18 | -376.27 | 205.42 | 23.35 | -326.50 | -863.38 | 0.003 | 0.014 | 78.57 |
| 38 | 20 | -89.45 | 397.97 | 758.55 | 3.22 | 469.65 | 4.95 | 0.0044 | n.a. | n.a. |
| | 25 | 271.53 | -203.87 | 954.62 | 21.19 | 443.65 | -121.54 | 0.0038 | 0.0124 | 69.35 |
| 39 | 20 | 112.89 | 965.50 | 915.13 | -9.93 | 486.39 | 313.76 | 0.0025 | n.a. | n.a. |
| 40 | 25 | 483.24 | -292.57 | 667.77 | 46.82 | 547.78 | -161.42 | 0.0059 | 0.007 | 15.71 |
| 41 | 20 | 627.34 | -15.42 | 333.06 | 10.31 | 101.11 | 513.44 | 0.0038 | n.a. | n.a. |
| 42 | 20 | 654.91 | -417.43 | 638.01 | -28.46 | 231.67 | -637.55 | 0.0065 | n.a. | n.a. |
| | 30 | -905.84 | 599.03 | 332.29 | 82.71 | -239.02 | -345.02 | 0.0062 | n.a. | n.a. |
| | 40 | 14.53 | -596.59 | 383.38 | 98.85 | -713.92 | 821.40 | 0.0092 | n.a. | n.a. |
| 43 | 20 | 257.00 | 7.36 | 397.29 | -30.35 | 175.55 | 164.65 | 0.0084 | n.a. | n.a. |
| | 30 | -286.77 | -275.73 | 425.07 | 10.20 | 706.93 | -730.17 | 0.0094 | n.a. | n.a. |
| | 40 | -166.81 | 631.01 | 336.19 | 23.81 | 221.83 | 57.17 | 0.0093 | n.a. | n.a. |
| | 50 | 371.38 | -88.75 | 364.31 | -4.65 | 664.28 | -70.84 | 0.0080 | n.a. | n.a. |
| 44 | 40 | -863.78 | 250.57 | 917.61 | 177.88 | 599.91 | -623.89 | 0.0024 | n.a. | n.a. |
| | 45 | -960.33 | 709.12 | 811.10 | 163.79 | 697.25 | -635.20 | 0.0030 | n.a. | n.a. |
| | 50 | -774.49 | 605.92 | 895.73 | 173.68 | 434.69 | -440.50 | 0.0023 | n.a. | n.a. |
| | 55 | 227.19 | -372.61 | 816.50 | 520.24 | 598.95 | -138.87 | 0.0043 | n.a. | n.a. |
| | 60 | -623.59 | 541.96 | 666.63 | 675.63 | 464.76 | -267.26 | 0.0010 | n.a. | n.a. |
| 45 | 25 | -607.03 | 832.04 | 810.14 | -13.72 | 463.53 | -415.35 | 0.0040 | n.a. | n.a. |
| 46 | 25 | -427.92 | 490.34 | 890.04 | -10.86 | 618.91 | -284.37 | 0.0030 | n.a. | n.a. |
| 47 | 25 | -878.57 | 633.02 | 221.97 | 28.01 | -140.95 | -139.73 | 0.0055 | n.a. | n.a. |
| 48 | 25 | 790.73 | -232.30 | 506.54 | 53.31 | -135.51 | 402.76 | 0.0096 | n.a. | n.a. |
| 49 | 25 | 81.40 | 806.13 | 578.90 | 62.15 | 155.70 | 388.39 | 0.0082 | n.a. | n.a. |
| 50 | 25 | 576.73 | 321.30 | 329.73 | -2.76 | 558.85 | 760.08 | 0.007 | 0.008 | 12.50 |
| 51 | 25 | -462.46 | 93.81 | 347.58 | 77.10 | -52.74 | -279.53 | 0.007 | 0.008 | 12.50 |
| 52 | 25 | -486.85 | 154.48 | 370.28 | 19.15 | 137.89 | -323.82 | 0.004 | 0.007 | 42.86 |
| 53 | 25 | 79.71 | -190.39 | 420.98 | 20.11 | -139.16 | 57.26 | 0.0043 | n.a. | n.a. |
| **average rmsd** | | | | | | | | **0.0059** | **0.0074** | **20.27** |

[a] bounds -1000 and 2000; n.a.: not available/not applicable.

Table 2.11 UNIQUAC binary interaction parameters without closure equations for quaternary aromatic extraction systems at 25°C (r=40°C)

| System No. | Binary Interaction Parameters (K) | | | | | | rmsd |
|---|---|---|---|---|---|---|---|
| | $A_{12}$ | $A_{13}$ | $A_{14}$ | $A_{23}$ | $A_{24}$ | $A_{34}$ | |
| | $A_{21}$ | $A_{31}$ | $A_{41}$ | $A_{32}$ | $A_{42}$ | $A_{43}$ | |
| 54 | 625.32 | -325.40 | 240.71 | 403.68 | 417.04 | 969.31 | 0.011 |
| | 537.36 | 85.26 | 107.30 | 508.71 | 690.34 | -341.44 | |
| 55 | 510.57 | -401.54 | 674.58 | -345.98 | 29.01 | 161.68 | 0.007 |
| | -10.05 | 197.45 | 27.65 | 514.90 | 468.77 | -245.87 | |

(*continued on next page*)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 56 | -288.47 | 203.16 | 145.88 | 3.14 | 980.97 | -20.99 | 0.008 |
| | 672.54 | -25.23 | 822.64 | -51.15 | -205.62 | 335.28 | |
| 57 | -250.96 | 629.03 | 309.49 | 681.66 | 228.86 | 197.57 | 0.009 |
| | 701.46 | 822.52 | 185.30 | 579.95 | 523.04 | 940.12 | |
| 58 | 566.93 | 468.94 | 278.19 | -155.89 | 242.84 | 161.06 | 0.009 |
| | -155.90 | -170.99 | 539.31 | 333.30 | 179.71 | -17.53 | |
| 59 | -603.58 | 891.13 | 450.30 | 212.63 | 450.82 | 158.20 | 0.007 |
| | -569.41 | -692.55 | 437.84 | -593.29 | -275.18 | 17.92 | |
| 60 | 512.60 | 405.78 | 222.07 | 884.19 | 503.49 | -38.73 | 0.008 |
| | -204.94 | 85.44 | 201.84 | 21.45 | 89.72 | 630.17 | |
| 61 | -389.97 | 57.71 | 281.53 | -415.98 | 584.57 | 47.65 | 0.008 |
| | 413.75 | 311.27 | 185.48 | -73.87 | -88.71 | -35.51 | |
| 62 | -773.08 | 572.23 | 420.83 | 930.53 | -85.617 | 308.86 | 0.006 |
| | 30.60 | 426.04 | -91.85 | 11.39 | -648.63 | -508.51 | |
| 62[r] | 256.62 | 756.55 | 539.77 | 567.09 | 524.63 | 310.96 | 0.006 |
| | -198.89 | 734.36 | -134.43 | 346.42 | -244.97 | 474.00 | |
| **average rmsd** | | | | | | | **0.0079** |

Table 2.12 UNIQUAC binary interaction parameters without closure equations for quinary aromatic extraction systems at 25 °C

| **System No.** | **Binary Interaction Parameters (K)** | | | | | **rmsd** |
|---|---|---|---|---|---|---|
| | $A_{12}$ | $A_{21}$ | $A_{31}$ | $A_{41}$ | $A_{51}$ | |
| | $A_{13}$ | $A_{23}$ | $A_{32}$ | $A_{42}$ | $A_{52}$ | |
| | $A_{14}$ | $A_{24}$ | $A_{34}$ | $A_{43}$ | $A_{53}$ | |
| | $A_{15}$ | $A_{25}$ | $A_{35}$ | $A_{45}$ | $A_{54}$ | |
| 63 | -887.07 | -264.16 | 597.93 | 936.08 | 883.80 | 0.019 |
| | 74.69 | -400.40 | 945.18 | -427.55 | -404.10 | |
| | -266.39 | 321.14 | 47.70 | 246.50 | -49.68 | |
| | -97.53 | 912.75 | 664.69 | 192.11 | 116.41 | |
| 64 | -780.64 | -257.75 | -137.81 | -19.48 | 11.63 | 0.011 |
| | -231.69 | -442.54 | -169.34 | -187.94 | -92.19 | |
| | 65.66 | -90.12 | -96.84 | 763.18 | -118.00 | |
| | 558.55 | 137.40 | -76.20 | 241.08 | 40.58 | |
| 65 | 494.50 | -788.04 | 123.41 | -72.94 | 892.06 | 0.010 |
| | 894.92 | 378.75 | 932.81 | 197.94 | 109.16 | |
| | -296.96 | -75.08 | 173.44 | 951.70 | 592.68 | |
| | 86.66 | 520.22 | 688.35 | 115.58 | 22.09 | |
| **average rmsd** | | | | | | **0.0133** |

The results of UNIQUAC parameter estimation along with the corresponding percentage gain values for the ternary systems are given in Table 2.10. It is seen that the rmsd values obtained using GA are less than those reported in the literature; approximately 20 percent better. The results of UNIQUAC parameter estimation for quaternary and quinary systems are given in Table 2.11 and Table 2.12 respectively. Good agreement between the experimental tie-line compositions and the tie-line compositions predicted by UNIQUAC model can be seen from their rmsd values. This would mean, for quaternary and quinary systems also the parameters that are obtained using GA predict the LLE more accurately for UNIQUAC model.

### 2.3.2 Hydrogen bonding systems

Prediction of liquid-liquid equilibria significantly affected by the hydrogen bonds in hydrogen bonding systems; predicted values of $r$ and $q$ for alcohols, ethers and oxygen containing systems show respectively 2.5 – 20 percent and 5 – 20 percent deviation from the literature values [45]. Hydrogen bonding systems considered for our estimation is given in Table 2.13.

Table 2.13 Hydrogen bonding systems at different temperatures used for parameter estimation

| System No. | System Name | Temperature (°C) | Reference |
|---|---|---|---|
| | **Ternary Systems** | | |
| 1 | water(1)-methanol(2)-1,4-dicyanobutane(3) | 25 | [46] |
| 2 | water(1)-ethanol(2)-1,4-dicyanobutane(3) | 25 | [46] |
| 3 | water(1)-1-propanol(2)-1,4-dicyanobutane(3) | 25 | [46] |
| 4 | water(1)-methanol(2)-butanenitrile(3) | 25 | [46] |
| 5 | water(1)-ethanol(2)-butanenitrile(3) | 25 | [46] |
| 6 | water(1)-1-propanol(2)-butanenitrile(3) | 25 | [46] |
| 7 | water(1)-methanol(2)-benzonitrile(3) | 25 | [46] |
| 8 | water(1)-ethanol(2)-benzonitrile(3) | 25 | [46] |
| 9 | water(1)-1-propanol(2)-benzonitrile(3) | 25 | [46] |
| 10 | furfural(1)-chlorobenzene(2)-*n*-hexane(3) | 25 | [47] |
| 11 | furfural(1)-1,2-dichlorobenzene(2)-*n*-hexane(3) | 25 | [47] |
| 12 | furfural(1)-1,3-dichlorobenzene(2)-*n*-hexane(3) | 25 | [47] |
| 13 | furfural(1)-1,2,4-trichlorobenzene(2)-*n*-hexane(3) | 25 | [47] |
| 14 | furfural(1)-chlorobenzene(2)-*n*-dodecane(3) | 25 | [47] |
| 15 | furfural(1)-chlorobenzene(2)-*n*-hexadecane(3) | 25 | [47] |
| 16 | furfural(1)-1,2-dichlorobenzene(2)-*n*-hexadecane(3) | 25 | [47] |
| 17 | furfural(1)-1,3-dichlorobenzene(2)-*n*-hexadecane(3) | 25 | [47] |
| 18 | furfural(1)-1,2,4-trichlorobenzene(2)-*n*-hexadecane(3) | 25 | [47] |

*(continued on next page)*

| | | | |
|---|---|---|---|
| 19 | furfuryl alcohol(1)-benzene(2)-hexane(3) | 25 | [48] |
| 20 | furfuryl alcohol(1)-methylbenzene(2)-hexane(3) | 25 | [48] |
| 21 | furfuryl alcohol(1)-1,2-dimethylbenzene(2)-hexane(3) | 25 | [48] |
| 22 | furfuryl alcohol(1)-benzene(2)-dodecane(3) | 25 | [48] |
| 23 | furfuryl alcohol(1)-methylbenzene(2)-dodecane(3) | 25 | [48] |
| 24 | furfuryl alcohol(1)-1,2-dimethylbenzene(2)-dodecane(3) | 25 | [48] |
| 25 | furfuryl alcohol(1)-benzene(2)-hexadecane(3) | 25 | [48] |
| 26 | furfuryl alcohol(1)-methylbenzene(2)-hexadecane(3) | 25 | [48] |
| 27 | furfuryl alcohol(1)-1,2-dimethylbenzene(2)-hexadecane(3) | 25 | [48] |
| 28 | *n*-hexane(1)-benzene(2)-1,4-dicyanobutane(3) | 25 | [49] |
| 29 | *n*-hexane(1)-methylbenzene(2)-1,4-dicyanobutane(3) | 25 | [49] |
| 30 | *n*-hexane(1)-1,2-dimethylbenzene(2)-1,4-dicyanobutane(3) | 25 | [49] |
| 31 | *n*-hexane(1)-1,3-dimethylbenzene(2)-1,4-dicyanobutane(3) | 25 | [49] |
| 32 | *n*-hexane(1)-1,4-dimethylbenzene(2)-1,4-dicyanobutane(3) | 25 | [49] |
| 33 | *n*-hexane(1)-1,3,5-trimethylbenzene(2)-1,4-dicyanobutane(3) | 25 | [49] |
| 34 | *n*-hexane(1)-ethylbenzene(2)-1,4-dicyanobutane(3) | 25 | [49] |
| 35 | *n*-nonane(1)-benzene(2)-1,4-dicyanobutane(3) | 25 | [49] |
| 36 | *n*-dodecane(1)-benzene(2)-1,4-dicyanobutane(3) | 25 | [49] |
| 37 | *n*-hexadecane(1)-benzene(2)-1,4-dicyanobutane(3) | 25 | [49] |
| 38 | hexadecane(1)-benzene(2)-1,3-dimethyl-2-imidazolidinone(3) | 25 | [50] |
| 39 | hexadecane(1)-toluene(2)-1,3-dimethyl-2-imidazolidinone(3) | 25 | [50] |
| 40 | hexadecane(1)-*o*-xylene(2)-1,3-dimethyl-2-imidazolidinone(3) | 25 | [50] |
| 41 | hexadecane(1)-*m*-xylene(2)-1,3-dimethyl-2-imidazolidinone(3) | 25 | [50] |
| 42 | hexadecane(1)-*p*-xylene(2)-1,3-dimethyl-2-imidazolidinone(3) | 25 | [50] |
| 43 | hexadecane(1)-mesitylene(2)-1,3-dimethyl-2-imidazolidinone(3) | 25 | [50] |
| 44 | hexadecane(1)-ethylbenzene(2)-1,3-dimethyl-2-imidazolidinone(3) | 25 | [50] |
| 45 | tetradecane(1)-benzene(2)-1,3-dimethyl-2-imidazolidinone(3) | 25 | [50] |
| 46 | tetradecane(1)-toluene(2)-1,3-dimethyl-2-imidazolidinone(3) | 25 | [50] |
| 47 | tetradecane(1)-mesitylene(2)-1,3-dimethyl-2-imidazolidinone(3) | 25 | [50] |
| 48 | tetradecane(1)-ethylbenzene(2)-1,3-dimethyl-2-imidazolidinone(3) | 25 | [50] |
| 49 | methyl *tert*-butyl ether(1)-ethanol(2)-water(3) | 15, 25 | [51] |
| 50 | methyl *tert*-butyl ether(1)-1-hexanol(2)-water(3) | 15, 25, 35 | [51] |
| 51 | epichlorohydrin(1)-water(2)-methanol(3) | 0 | [52] |
| 52 | allyl chloride(1)-water(2)-methanol(3) | 0 | [52] |
| 53 | water(1)-methanol(2)-methylal(3) | 0, 20, 40 | [53] |
| 54 | dodecane(1)-propylbenzene(2)-N-methyl-2-pyrrolidone(3) | 25, 35, 45, 55 | [54] |
| 55 | tetradecane(1)-propylbenzene(2)-N-methyl-2-pyrrolidone(3) | 25, 35, 45, 55 | [54] |
| 56 | heptadecane(1)-propylbenzene(2)-N-methyl-2-pyrrolidone(3) | 25, 35, 45, 55 | [54] |
| 57 | HFE-7100®(1)-water(2)-ethanol(3) | 25, 35 | [55] |
| 58 | 2-propanone(1)-glycerol(2)-methanol(3) | 10, 20, 30 | [56] |
| 59 | 2-butanone(1)-glycerol(2)-ethanol(3) | 10, 20, 30 | [56] |
| 60 | 2-butanone(1)-glycerol(2)-2-propanol(3) | 10, 20, 30 | [56] |
| 61 | 2-methoxy-2-methylpropane(1)-ethanol(2)-water(3) | 25 | [57] |
| 62 | 2-methoxy-2-methylpropane(1)-1-octanol(2)-water(3) | 25 | [57] |
| 63 | 1-octanol(1)-ethanol(2)-water(3) | 25 | [57] |
| | **Quaternary Systems** | | |
| 64 | 1-octanol(1)-2-methoxy-2-methylpropane(2)-water(3)-ethanol(4) | 25 | [57] |
| 65 | 1-octanol(1)-2-methoxy-2-methylbutane(2)-water(3)-methanol(4) | 25 | [58] |

The parameters α, $r$, and $q$ as given in Table A.2 and A.3 of Appendix A have been taken from corresponding literature. The results of parameter estimation along with the corresponding percentage gain values are given in Table 2.14-2.16.

Table 2.14 NRTL binary interaction parameters for ternary hydrogen bonding systems at different temperatures

| System No. | Temp. (°C) | Binary Interaction Parameters (K) | | | | | | rmsd | rmsd [lit] | $gain_{lit}^{ga}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $A_{12}$ | $A_{21}$ | $A_{13}$ | $A_{31}$ | $A_{23}$ | $A_{32}$ | | | |
| 1 | 25 | 606.12 | -68.47 | 1501.00 | 196.54 | 97.65 | 733.13 | 0.003 | 0.011 | 72.73 |
| 2 | 25 | 250.95 | 68.01 | 1932.60 | 1962.10 | 8.99 | 620.33 | 0.004 | 0.007 | 42.86 |
| 3 | 25 | 434.87 | -82.76 | 1225.40 | 185.88 | -358.62 | 492.71 | 0.002 | 0.013 | 84.62 |
| 4 | 25 | 1390.70 | -26.46 | 1442.00 | 524.46 | 59.32 | 1337.00 | 0.003 | 0.014 | 78.57 |
| 5 | 25 | 370.04 | -374.48 | 1209.30 | 568.90 | 538.41 | -690.97 | 0.006 | 0.014 | 57.14 |
| 6 | 25 | 986.72 | -222.50 | 1166.40 | 516.39 | -94.43 | 501.67 | 0.003 | 0.008 | 62.50 |
| 7 | 25 | 1064.20 | 705.91 | 1792.90 | 664.27 | 284.29 | 1389.70 | 0.006 | 0.010 | 40.00 |
| 8 | 25 | 1148.00 | -7.94 | 1651.10 | 729.88 | 198.29 | 987.45 | 0.003 | 0.014 | 78.57 |
| 90 | 25 | 495.70 | 265.34 | 1637.20 | 736.98 | -282.92 | 829.02 | 0.003 | 0.007 | 57.14 |
| 10 | 25 | 22.96 | 309.55 | 627.68 | 846.89 | -159.02 | 256.47 | 0.002 | 0.007 | 71.43 |
| 11 | 25 | 1725.80 | -64.95 | 634.17 | 805.71 | -19.78 | 1623.30 | 0.002 | 0.009 | 77.78 |
| 12 | 25 | 1420.00 | -69.04 | 620.37 | 904.21 | 22.28 | 1283.30 | 0.003 | 0.009 | 66.67 |
| 13 | 25 | 1032.50 | -11.89 | 592.63 | 736.92 | 124.36 | 735.30 | 0.002 | 0.009 | 77.78 |
| 14 | 25 | 1261.10 | 318.56 | 756.76 | 656.42 | 665.30 | 1272.00 | 0.003 | 0.007 | 57.14 |
| 15 | 25 | 450.64 | 269.20 | 1201.60 | 725.42 | 543.54 | 150.27 | 0.001 | 0.009 | 88.89 |
| 16 | 25 | 1138.50 | 167.13 | 1288.30 | 837.75 | 439.26 | 938.02 | 0.002 | 0.006 | 66.67 |
| 17 | 25 | 1209.90 | 171.06 | 1155.40 | 846.01 | 657.38 | 856.96 | 0.002 | 0.005 | 60.00 |
| 18 | 25 | 1074.60 | 203.39 | 1057.10 | 725.48 | 582.95 | 749.49 | 0.001 | 0.006 | 83.33 |
| 19 | 25 | 629.47 | 731.48 | 1014.20 | 1110.90 | 931.00 | 486.40 | 0.002 | 0.005 | 60.00 |
| 20 | 25 | 630.89 | 760.53 | 1015.00 | 1094.40 | 987.51 | 531.28 | 0.003 | 0.003 | 0.00 |
| 21 | 25 | 708.25 | 700.75 | 1038.40 | 1138.90 | 1130.50 | 566.54 | 0.002 | 0.004 | 50.00 |
| 22 | 25 | 575.89 | 776.61 | 1462.30 | 1298.80 | 723.81 | 1312.90 | 0.004 | 0.004 | 0.00 |
| 23 | 25 | 692.48 | 746.79 | 1323.80 | 1178.90 | 735.67 | 1134.20 | 0.004 | 0.004 | 0.00 |
| 24 | 25 | 682.58 | 723.88 | 1273.70 | 1196.60 | 746.62 | 1126.40 | 0.004 | 0.004 | 0.00 |
| 25 | 25 | 382.47 | 831.51 | 1522.30 | 1425.80 | 835.03 | 1366.80 | 0.004 | 0.006 | 33.33 |
| 26 | 25 | 571.27 | 793.17 | 1595.50 | 1372.40 | 785.77 | 1336.10 | 0.003 | 0.005 | 40.00 |
| 27 | 25 | 541.43 | 838.76 | 1511.00 | 1433.70 | 837.77 | 960.20 | 0.003 | 0.005 | 40.00 |
| 28 | 25 | 564.10 | 722.24 | 1666.10 | 777.69 | 595.72 | 667.90 | 0.003 | 0.004 | 25.00 |
| 29 | 25 | 583.48 | 998.81 | 1731.20 | 786.94 | 564.41 | 798.44 | 0.005 | 0.006 | 16.67 |
| 30 | 25 | 505.66 | 1251.90 | 1688.30 | 786.03 | 559.16 | 751.49 | 0.004 | 0.005 | 20.00 |
| 31 | 25 | 242.03 | 1683.40 | 1440.30 | 711.35 | 645.80 | 586.16 | 0.004 | 0.005 | 20.00 |
| 32 | 25 | -475.42 | 154.33 | 1319.10 | 758.54 | 919.46 | -172.81 | 0.004 | 0.004 | 0.00 |
| 33 | 25 | -796.38 | 637.89 | 1620.90 | 671.91 | 707.95 | 69.43 | 0.006 | 0.006 | 0.00 |
| 34 | 25 | -421.86 | 929.71 | 1563.50 | 723.60 | 656.02 | 95.02 | 0.004 | 0.005 | 20.00 |
| 35 | 25 | 135.31 | 857.02 | 1913.40 | 1272.30 | 677.88 | 301.56 | 0.003 | 0.005 | 40.00 |
| 36 | 25 | 1283.00 | 870.58 | 1586.70 | 1370.20 | 786.04 | 1768.10 | 0.007 | 0.005 | -40.00 |
| 37 | 25 | 1339.10 | 997.89 | 1652.50 | 1685.80 | 864.96 | 1731.30 | 0.007 | 0.005 | -40.00 |
| 38 | 25 | -410.43 | 680.97 | 1273.20 | 1536.00 | 771.10 | -84.40 | 0.002 | 0.004 | 50.00 |
| | | | | | | | | | | |

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| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 39 | 25 | 215.24 | 844.31 | 1159.80 | 1257.40 | 685.32 | 818.63 | 0.003 | 0.009 | 66.67 |
| 40 | 25 | 180.61 | 1699.30 | 1744.80 | 1225.00 | 754.64 | 392.93 | 0.004 | 0.006 | 33.33 |
| 41 | 25 | 435.78 | 738.96 | 1261.00 | 1250.20 | 680.06 | 751.99 | 0.002 | 0.012 | 83.33 |
| 42 | 25 | 1905.60 | -72.64 | 1332.30 | 1369.70 | 629.70 | 843.51 | 0.002 | 0.013 | 84.62 |
| 43 | 25 | 93.54 | 234.32 | 1161.60 | 1444.40 | 432.91 | 270.88 | 0.002 | 0.009 | 77.78 |
| 44 | 25 | -103.60 | 75.73 | 1077.00 | 1429.20 | 391.15 | 274.90 | 0.003 | 0.017 | 82.35 |
| 45 | 25 | 649.41 | 676.45 | 1959.60 | 1719.10 | 548.97 | 838.56 | 0.008 | 0.013 | 38.46 |
| 46 | 25 | 542.58 | -7.22 | 891.58 | 1966.50 | 1859.50 | 1084.20 | 0.010 | 0.018 | 44.44 |
| 47 | 25 | 211.27 | 512.38 | 1275.30 | 1957.50 | 490.40 | 518.54 | 0.007 | 0.005 | -40.00 |
| 48 | 25 | 350.50 | 543.14 | 1354.80 | 1976.80 | 491.19 | 585.01 | 0.007 | 0.010 | 30.00 |
| 49 | 15 | 239.35 | 298.99 | 562.03 | 1052.80 | -277.93 | 1002.50 | 0.0044 | n.a. | n.a. |
| | 25 | -572.88 | 585.61 | 604.10 | 1040.80 | -278.03 | 342.98 | 0.0068 | n.a. | n.a. |
| 50 | 15 | -51.37 | -56.94 | 626.92 | 1968.10 | 192.37 | 1733.30 | 0.0055 | n.a. | n.a. |
| | 25 | -494.29 | -383.36 | 652.60 | 1814.90 | 256.72 | 1957.30 | 0.0032 | n.a. | n.a. |
| | 35 | 350.71 | -991.55 | 552.19 | 1244.30 | 34.96 | 1378.50 | 0.0051 | n.a. | n.a. |
| 51 | 0 | 524.48 | 1410.30 | -182.01 | 593.99 | 1373.20 | -715.04 | 0.0075 | 0.0139 | 46.04 |
| 52 | 0 | 805.58 | 1693.10 | 816.57 | 280.67 | 351.08 | 1560.60 | 0.0065 | 0.0335 | 80.60 |
| 53 | 0 | -130.93 | -38.59 | 669.44 | -776.33 | 445.08 | 563.59 | 0.0038 | n.a. | n.a. |
| | 20 | -144.32 | 216.67 | -246.41 | 97.10 | 412.10 | 622.80 | 0.0022 | n.a. | n.a. |
| | 40 | 1784.00 | -446.74 | -625.77 | 627.09 | 386.34 | 717.59 | 0.0018 | n.a. | n.a. |
| 54 | 25 | 163.11 | 360.08 | 171.59 | 840.77 | 84.66 | 501.86 | 0.0020 | 0.0025 | 20.00 |
| | 35 | 897.50 | -31.58 | 120.92 | 944.04 | -137.72 | 969.36 | 0.0016 | 0.0020 | 20.00 |
| | 45 | 163.88 | 1208.00 | 181.95 | 770.79 | -144.98 | 1155.40 | 0.0029 | 0.0066 | 56.06 |
| | 55 | 829.76 | 174.19 | 38.38 | 929.93 | 576.84 | 471.40 | 0.0017 | 0.0032 | 46.88 |
| 55 | 25 | 213.36 | 75.46 | 121.04 | 1080.90 | 372.42 | 57.53 | 0.0024 | 0.0035 | 31.43 |
| | 35 | 1504.20 | 146.65 | 66.38 | 1120.30 | -190.37 | 1855.50 | 0.0030 | 0.0056 | 46.43 |
| | 45 | -65.79 | 416.19 | 41.33 | 1095.70 | -305.11 | 690.78 | 0.0019 | 0.0048 | 60.42 |
| | 55 | 873.99 | 370.82 | -26.67 | 1086.60 | -61.17 | 1322.80 | 0.0018 | 0.0052 | 65.38 |
| 56 | 25 | 128.76 | -303.51 | 441.12 | 1044.60 | 1958.20 | -590.90 | 0.0035 | 0.0023 | -52.17 |
| | 35 | -0.84 | -336.06 | 297.17 | 1252.20 | -154.28 | -118.80 | 0.0043 | 0.0040 | -7.50 |
| | 45 | -207.76 | -269.74 | 264.83 | 1201.80 | 1196.60 | -980.54 | 0.0037 | 0.0038 | 2.63 |
| | 55 | -325.20 | 1101.90 | 96.83 | 1213.80 | -430.90 | 975.88 | 0.0021 | 0.0022 | 4.55 |
| 57 | 25 | 1027.30 | 1892.20 | 541.85 | 547.45 | -237.65 | 1106.30 | 0.009 | 0.015 | 40.00 |
| | 35 | 964.42 | 1812.30 | 685.32 | 531.52 | 27.12 | 1468.80 | 0.009 | 0.012 | 25.00 |
| 58 | 10 | 848.02 | 195.05 | 1201.40 | 125.90 | 971.42 | 344.16 | 0.0049 | n.a. | n.a. |
| | 20 | 884.60 | 240.74 | -689.55 | 712.80 | -204.34 | -76.81 | 0.0020 | n.a. | n.a. |
| | 30 | 849.16 | 229.55 | -560.85 | 786.73 | -101.52 | 6.80 | 0.0024 | n.a. | n.a. |
| 59 | 10 | 1085.80 | 413.38 | 489.02 | 189.76 | 891.98 | -37.68 | 0.0026 | n.a. | n.a. |
| | 20 | 1013.60 | 469.83 | 630.25 | -157.80 | 685.54 | -106.58 | 0.0015 | n.a. | n.a. |
| | 30 | 936.41 | 451.39 | 1533.50 | 172.34 | 1882.80 | -40.97 | 0.0022 | n.a. | n.a. |
| 60 | 10 | 1109.20 | 424.27 | 51.52 | 381.56 | 804.85 | -85.79 | 0.0016 | n.a. | n.a. |
| | 20 | 1025.50 | 436.93 | 687.67 | -410.70 | 553.32 | -85.36 | 0.0023 | n.a. | n.a. |
| | 30 | 1014.60 | 452.52 | 788.92 | -462.23 | 569.46 | -95.55 | 0.0026 | n.a. | n.a. |
| 61 | 25 | 502.83 | -141.23 | 599.77 | 1494.10 | 22.44 | 381.46 | 0.0019 | 0.0052 | 63.46 |
| 62 | 25 | -433.94 | -532.52 | 697.37 | 1929.20 | 238.44 | 1584.40 | 0.0045 | 0.0047 | 4.26 |
| 63 | 25 | 1192.30 | 683.70 | 344.84 | 1960.40 | -133.50 | 1759.10 | 0.0026 | 0.0209 | 87.56 |
| **average rmsd** | | | | | | | | **0.0036** | **0.0078** | **53.85** |

n.a.: not available/not applicable

Table 2.15 UNIQUAC binary interaction parameters for ternary hydrogen bonding systems at different temperatures

| System No. | Temp. (°C) | Binary Interaction Parameters (K) | | | | | | rmsd | rmsd [lit] | $gain_{lit}^{ga}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $A_{12}$ | $A_{21}$ | $A_{13}$ | $A_{31}$ | $A_{23}$ | $A_{32}$ | | | |
| 1 | 25 | 803.64 | -455.85 | 180.83 | 245.49 | 449.52 | 209.27 | 0.005 | 0.016 | 68.75 |
| 2 | 25 | -606.03 | -286.55 | 160.67 | 272.24 | -145.85 | 267.09 | 0.003 | 0.011 | 72.73 |
| 3 | 25 | -579.49 | -440.55 | 114.23 | 312.87 | 5.49 | -445.88 | 0.003 | 0.028 | 89.29 |
| 4 | 25 | 428.04 | -453.46 | 257.38 | 391.28 | -17.66 | 260.60 | 0.004 | 0.013 | 69.23 |
| 5 | 25 | -756.42 | -51.48 | 191.26 | 438.21 | -7.89 | 41.04 | 0.009 | 0.019 | 52.63 |
| 6 | 25 | -333.82 | -480.64 | 252.69 | 415.09 | -227.67 | -101.42 | 0.005 | 0.012 | 58.33 |
| 7 | 25 | 952.88 | -517.56 | 349.97 | 528.30 | 212.57 | 265.08 | 0.006 | 0.019 | 68.42 |
| 8 | 25 | 725.68 | -599.16 | 613.47 | 490.80 | 120.99 | -82.03 | 0.006 | 0.018 | 66.67 |
| 9 | 25 | -636.22 | -487.27 | 277.43 | 586.34 | 75.38 | -858.04 | 0.007 | 0.010 | 30.00 |
| 10 | 25 | 179.11 | -66.83 | 11.51 | 541.38 | -280.42 | 571.48 | 0.005 | 0.011 | 54.55 |
| 11 | 25 | -338.94 | -65.71 | 12.86 | 446.78 | -179.82 | -231.70 | 0.003 | 0.010 | 70.00 |
| 12 | 25 | 259.21 | -8.82 | 16.59 | 435.97 | 110.16 | 38.89 | 0.004 | 0.012 | 66.67 |
| 13 | 25 | -185.11 | 292.12 | 19.78 | 478.87 | -272.99 | 387.62 | 0.007 | 0.016 | 56.25 |
| 14 | 25 | 175.06 | 263.51 | -69.23 | 494.19 | 62.11 | 225.49 | 0.005 | 0.011 | 54.55 |
| 15 | 25 | 168.64 | -63.12 | 162.62 | 342.73 | -199.96 | 356.81 | 0.007 | 0.012 | 41.67 |
| 16 | 25 | 455.58 | -148.56 | 203.59 | 349.63 | -229.46 | 556.36 | 0.006 | 0.013 | 53.85 |
| 17 | 25 | -159.29 | 134.88 | -16.95 | 499.57 | 299.54 | -303.19 | 0.005 | 0.013 | 61.54 |
| 18 | 25 | 905.43 | 549.53 | -47.84 | 450.05 | 156.80 | 837.26 | 0.012 | 0.011 | -9.09 |
| 19 | 25 | 365.45 | -197.19 | -14.21 | 815.32 | -338.11 | 797.32 | 0.004 | 0.020 | 80.00 |
| 20 | 25 | -407.42 | 132.12 | -25.93 | 441.96 | 101.36 | -521.06 | 0.012 | 0.020 | 40.00 |
| 21 | 25 | 622.19 | -12.75 | 52.52 | 486.44 | 728.62 | 112.61 | 0.007 | 0.020 | 65.00 |
| 22 | 25 | 214.81 | 74.78 | -22.05 | 503.85 | 295.43 | -41.78 | 0.008 | 0.030 | 73.33 |
| 23 | 25 | -104.04 | 435.05 | -27.14 | 598.92 | -266.77 | 780.13 | 0.011 | 0.020 | 45.00 |
| 24 | 25 | -101.38 | 356.50 | -35.30 | 734.59 | -276.37 | 892.32 | 0.008 | 0.030 | 73.33 |
| 25 | 25 | 240.43 | 476.69 | -33.07 | 340.47 | 404.74 | 204.25 | 0.011 | 0.030 | 63.33 |
| 26 | 25 | 231.90 | 146.22 | -47.67 | 541.34 | 232.64 | 96.30 | 0.004 | 0.030 | 86.67 |
| 27 | 25 | 454.04 | 464.03 | -68.06 | 453.65 | 474.38 | 189.78 | 0.008 | 0.030 | 73.33 |
| 28 | 25 | 302.79 | 370.42 | 601.18 | 5.15 | 166.76 | 472.37 | 0.005 | 0.004 | -25.00 |
| 29 | 25 | -247.88 | 405.74 | 313.64 | 71.19 | 271.49 | -104.39 | 0.005 | 0.003 | -66.67 |
| 30 | 25 | 376.83 | -271.48 | 471.12 | 79.63 | 644.87 | -207.79 | 0.006 | 0.004 | -50.00 |
| 31 | 25 | -308.84 | 527.03 | 577.22 | 2.68 | 319.40 | -112.66 | 0.004 | 0.004 | 0.00 |
| 32 | 25 | -297.87 | 798.99 | 347.56 | 68.59 | 346.04 | -83.98 | 0.003 | 0.003 | 0.00 |
| 33 | 25 | -65.52 | -17.30 | 566.67 | -12.54 | 195.14 | -16.88 | 0.008 | 0.006 | -33.33 |
| 34 | 25 | -204.20 | 271.33 | 394.11 | 57.34 | 212.69 | -53.36 | 0.004 | 0.003 | -33.33 |
| 35 | 25 | 296.22 | -214.59 | 493.48 | 88.97 | 331.23 | -179.15 | 0.002 | 0.005 | 60.00 |
| 36 | 25 | 309.22 | -166.67 | 634.78 | 59.28 | -8.24 | 119.61 | 0.003 | 0.004 | 25.00 |
| 37 | 25 | 104.12 | -79.22 | 301.11 | 179.54 | 163.17 | -81.26 | 0.004 | 0.003 | -33.33 |
| 38 | 25 | -77.66 | -285.89 | 931.89 | 104.84 | -143.52 | -291.18 | 0.007 | 0.012 | 41.67 |
| 49 | 25 | 581.27 | -286.91 | 869.84 | -79.13 | 594.46 | -158.74 | 0.008 | 0.016 | 50.00 |
| 40 | 25 | 377.91 | 175.95 | 728.11 | -91.84 | 451.53 | 285.32 | 0.008 | 0.016 | 50.00 |
| 41 | 25 | -123.76 | 447.21 | 736.94 | -109.28 | 546.98 | -113.78 | 0.012 | 0.013 | 7.69 |

(*continued on next page*)

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 42 | 25 | -456.60 | 917.49 | 987.93 | -108.38 | 266.36 | -127.86 | 0.003 | 0.009 | 66.67 |
| 43 | 25 | -557.37 | 578.17 | 805.69 | -65.53 | 271.61 | -413.61 | 0.004 | 0.014 | 71.43 |
| 44 | 25 | -249.63 | 352.68 | 737.26 | 148.42 | -108.79 | 334.04 | 0.007 | 0.007 | 0.00 |
| 45 | 25 | 428.09 | -54.40 | 815.69 | -131.20 | 281.95 | 240.10 | 0.020 | 0.019 | -5.26 |
| 46 | 25 | 419.05 | -225.34 | 798.01 | -117.78 | 395.49 | -79.31 | 0.018 | 0.016 | -12.50 |
| 47 | 25 | 319.37 | 54.92 | 806.10 | -136.92 | 479.49 | 217.68 | 0.020 | 0.016 | -25.00 |
| 48 | 25 | 35.74 | -10.76 | 837.99 | -139.21 | 425.47 | -145.23 | 0.018 | 0.016 | -12.50 |
| 49 | 15 | 330.55 | -220.90 | 553.97 | 55.96 | 990.45 | -384.07 | 0.0039 | n.a. | n.a. |
| | 25 | 422.89 | -210.73 | 581.31 | 51.61 | 121.07 | -103.01 | 0.0034 | n.a. | n.a. |
| 50 | 15 | -170.62 | 385.74 | 396.99 | 131.75 | 253.42 | 58.84 | 0.0059 | n.a. | n.a. |
| | 25 | 282.91 | 198.49 | 393.20 | 330.71 | -31.59 | 745.16 | 0.0037 | n.a. | n.a. |
| | 35 | -97.04 | 530.80 | 376.74 | 313.58 | 75.32 | 228.59 | 0.0046 | n.a. | n.a. |
| 51 | 0 | 596.59 | 92.27 | 151.95 | 152.01 | 504.19 | -281.72 | 0.0088 | 0.0145 | 39.31 |
| 52 | 0 | 502.23 | 514.08 | 815.27 | -15.46 | 46.80 | 620.84 | 0.0042 | 0.0232 | 81.90 |
| 53 | 0 | 262.76 | -421.64 | -192.55 | -421.76 | 540.22 | -22.62 | 0.0022 | n.a. | n.a. |
| | 20 | 485.54 | -194.84 | -155.11 | -108.89 | 519.13 | -19.11 | 0.0020 | n.a. | n.a. |
| | 40 | -289.81 | -17.04 | -490.69 | -12.71 | 434.65 | 36.24 | 0.0039 | n.a. | n.a. |
| 54 | 25 | -18.04 | -27.17 | 236.97 | -8.11 | 28.02 | -40.06 | 0.0025 | 0.0024 | -4.17 |
| | 35 | 17.85 | 211.88 | 187.88 | 29.43 | -19.40 | 267.93 | 0.0033 | 0.0012 | -175.00 |
| | 45 | 189.66 | -187.72 | 269.48 | -29.38 | -132.47 | 108.77 | 0.0057 | 0.0046 | -23.91 |
| | 55 | 97.83 | 867.57 | 212.46 | -11.53 | 535.50 | 195.66 | 0.0043 | 0.0025 | -72.00 |
| 55 | 25 | -160.40 | 491.57 | 199.58 | 22.09 | 109.93 | 45.42 | 0.0034 | 0.0025 | -36.00 |
| | 35 | -535.73 | -186.21 | 162.00 | 57.79 | -61.14 | -706.91 | 0.0046 | 0.0055 | 16.36 |
| | 45 | -374.39 | -72.24 | 249.34 | -24.07 | 837.46 | -740.97 | 0.0062 | 0.0039 | -58.97 |
| | 55 | 125.77 | 473.10 | 211.25 | -7.02 | 235.84 | 313.06 | 0.0047 | 0.0047 | 0.00 |
| 56 | 25 | 799.34 | 128.13 | 358.93 | -64.97 | 899.61 | 615.31 | 0.0089 | 0.0022 | -304.55 |
| | 35 | -95.08 | 305.43 | 334.01 | -43.50 | 47.72 | 99.61 | 0.0079 | 0.0046 | -71.74 |
| | 45 | -67.37 | -186.64 | 338.07 | -47.54 | 428.81 | -528.79 | 0.0048 | 0.0043 | -11.63 |
| | 55 | 344.35 | -226.05 | 230.34 | 17.43 | -57.98 | 59.68 | 0.0046 | 0.0022 | -109.09 |
| 57 | 25 | 822.75 | 362.44 | 489.29 | -79.58 | 287.90 | -340.65 | 0.008 | 0.021 | 61.90 |
| | 35 | 919.16 | 161.21 | 385.41 | -32.45 | 123.21 | -548.87 | 0.008 | 0.019 | 57.89 |
| 58 | 10 | 257.83 | 134.41 | 381.40 | -231.97 | 282.63 | -191.14 | 0.0034 | 0.0061 | 44.26 |
| | 20 | 222.41 | 160.68 | -699.38 | 267.15 | -298.70 | -171.40 | 0.0026 | 0.0096 | 72.92 |
| | 30 | 221.00 | 148.67 | 515.60 | -96.21 | 686.11 | -153.58 | 0.0037 | 0.0054 | 31.48 |
| 59 | 10 | 329.68 | 135.12 | 435.80 | -260.17 | -0.98 | 65.01 | 0.0024 | 0.0091 | 73.63 |
| | 20 | 293.24 | 155.04 | -353.11 | 451.02 | 102.23 | -96.25 | 0.0030 | 0.0062 | 51.61 |
| | 30 | 479.42 | 105.63 | 669.72 | -347.69 | -208.47 | 349.78 | 0.0047 | 0.0064 | 26.56 |
| 60 | 10 | 350.03 | 120.89 | -386.58 | 379.28 | 44.47 | -36.93 | 0.0034 | 0.0073 | 53.42 |
| | 20 | 307.90 | 148.27 | -647.67 | 259.06 | -184.93 | -80.41 | 0.0047 | 0.0057 | 17.54 |
| | 30 | 334.66 | 135.42 | 595.45 | -301.45 | 176.83 | -36.05 | 0.0036 | 0.0051 | 29.41 |
| 61 | 25 | 531.21 | -241.77 | 539.80 | 109.04 | 897.78 | -231.59 | 0.0040 | 0.0087 | 54.02 |
| 62 | 25 | 355.05 | -193.89 | 595.96 | 72.64 | 650.84 | -97.57 | 0.0046 | 0.0019 | -142.11 |
| 63 | 25 | 353.43 | 108.79 | 311.16 | 101.54 | -4.28 | 617.26 | 0.0049 | 0.0066 | 25.76 |
| **average rmsd** | | | | | | | | **0.0061** | **0.0115** | **46.96** |

n.a.: not available/not applicable

Table 2.16 Quaternary binary interaction parameters for hydrogen bonding systems at 25 °C

| System No. | Parameters, without closure equations (K) | | | | | | rmsd | rmsd [lit] | $gain_{lit}^{ga}$ |
|---|---|---|---|---|---|---|---|---|---|
| | $A_{12}$ $A_{21}$ | $A_{13}$ $A_{31}$ | $A_{14}$ $A_{41}$ | $A_{23}$ $A_{32}$ | $A_{24}$ $A_{42}$ | $A_{34}$ $A_{43}$ | | | |
| **NRTL** | | | | | | | | | |
| 64 | 1548.50 | 276.58 | 1165.50 | 333.82 | 835.51 | 1793.70 | 0.0040 | 0.0277 | 85.56 |
| | -595.37 | 1552.40 | 1010.70 | 1037.80 | 947.98 | -77.95 | | | |
| 65 | -847.34 | 191.92 | 334.69 | 466.31 | 433.20 | 608.37 | 0.0058 | 0.0345 | 83.19 |
| | 1160.20 | 1572.70 | 460.14 | 1186.40 | 326.94 | 99.46 | | | |
| **average rmsd** | | | | | | | **0.0049** | **0.0311** | **84.24** |
| **UNIQUAC** | | | | | | | | | |
| 64 | 84.11 | 264.42 | 94.42 | 232.15 | 904.18 | 279.31 | 0.0052 | 0.0180 | 71.11 |
| | 84.48 | 160.02 | 21.47 | 354.28 | -163.43 | -87.59 | | | |
| 65 | 417.54 | 374.12 | 35.67 | 520.57 | 71.17 | -10.47 | 0.0047 | 0.0106 | 55.66 |
| | -122.37 | 85.60 | 62.71 | 162.65 | 53.98 | -169.42 | | | |
| **average rmsd** | | | | | | | **0.0050** | **0.0143** | **65.03** |

It is seen that for hydrogen bonding systems too the rmsd values obtained using GA are less than those reported in the literature; approximately 54 percent and 84 percent better using NRTL model and 45 percent and 65 percent better using UNIQUAC model, respectively for ternary and quaternary systems. This clearly means that parameters obtained using GA will predict LLE more accurately than literature for any multicomponent systems.

It has been observed that for some cases, rmsd values reported in the literature are better than GA. The expected reason could be the biased experimental error in the reported LLE.

## 2.4 Conclusions

A genetic algorithm, which is a structured search-based optimization method, has been applied to estimate NRTL and UNIQUAC binary interaction parameters for liquid-liquid systems. Average root mean square deviation value is approximately 46 percent better for NRTL model and 40 percent better for UNIQUAC model, which is viewed as a potentially useful improvement for the prediction of liquid-liquid equilibria. The effect of using different genetic operators and their parameters has not been studied. Genetic algorithm can be applied to predict vapor-liquid equilibria.

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# Chapter 3

# ESTIMATION OF BINARY INTERACTION PARAMETERS WITH CLOSURE EQUATION/S

## 3.1 Introduction

The binary interaction parameters of UNIQUAC and NRTL activity coefficient models are expressed in terms of the difference of the respective interaction energies. The set of equations for ternary and higher component systems, with interaction energies as variables, is inconsistent for arbitrary values of binary interaction parameters [1]. Later Varheygi and Eon [2] stated that since the difference of energy interaction terms appears in the definition of binary interaction term used in the activity coefficient model, an addition of a constant value to each energy interaction term involved will cause no effect in the value of binary interaction parameters and hence in the calculated values of component activity coefficient. They therefore suggested that instead of estimating interaction parameters it would be better to estimate the interaction energies keeping the value of one interaction energy fixed at some arbitrary value. The interaction parameters calculated from these estimated interaction energies will not be all arbitrary but would be related to each other. Hala [1] showed that for a ternary system *i-j-k* there exist a linear relation between the binary interaction parameters and is of the form,

$$(\tau_{jk} - \tau_{kj}) = (\tau_{ik} - \tau_{ki}) - (\tau_{ij} - \tau_{ji}) \qquad (3.1)$$

This relationship is referred as "**closure equation**" [3]. The number of such independent relationship for a $c$ component system is $0.5 \times c(c-3)+1$ [1]. In this chapter, the binary interaction parameters have been estimated using GA, with closure equation/s (wce). The results thus obtained are compared with those reported in chapter 2 (without implementation of closure equation/s (woce)) and reported in the literature.

## 3.2 Theory and Calculation

### 3.2.1 Closure Equation/s

Ahmad [3] derived the closure equation/s for ternary, quaternary and quinary systems. The number of closure equation is one for ternary, three for quaternary and six for quinary system.

3.2.1.1 Ternary Systems

A ternary system has the following six binary interaction parameters $A_{12}, A_{21}; A_{13}, A_{31};$ and $A_{23}, A_{32}$. Closure equation which describes the relationship between these six binary interaction parameters is [4],

$$A_{12} - A_{21} + A_{23} - A_{32} + A_{31} - A_{13} = 0 \tag{3.2}$$

That is only five out of six binary interaction parameters are independent.

3.2.1.2 Quaternary Systems

For a quaternary system, the twelve binary interaction parameters are $A_{12}, A_{21}; A_{13}, A_{31}; A_{14}, A_{41}; A_{23}, A_{32}; A_{24}, A_{42};$ and $A_{34}, A_{43}$. Three closure equations for the quaternary systems are [4],

$$A_{12} - A_{21} + A_{23} - A_{32} + A_{31} - A_{13} = 0 \tag{3.3}$$

$$A_{12} - A_{21} + A_{24} - A_{42} + A_{41} - A_{14} = 0 \tag{3.4}$$

$$A_{23} - A_{32} + A_{34} - A_{43} + A_{42} - A_{24} = 0 \tag{3.5}$$

That is only nine out of twelve binary interaction parameters are independent.

3.2.1.3 Quinary Systems

A quinary system has the following twenty binary interaction parameters: $A_{12}, A_{21}; A_{13}, A_{31}; A_{14}, A_{41}; A_{15}, A_{51}; A_{23}, A_{32}; A_{24}, A_{42}; A_{25}, A_{52}; A_{34}, A_{43}; A_{35}, A_{53};$ and $A_{45}, A_{54}$. Six closure equations for quinary systems are [4],

$$A_{12} - A_{21} + A_{23} - A_{32} + A_{31} - A_{13} = 0 \tag{3.6}$$

$$A_{12} - A_{21} + A_{24} - A_{42} + A_{41} - A_{14} = 0 \tag{3.7}$$

$$A_{12} - A_{21} + A_{25} - A_{52} + A_{51} - A_{15} = 0 \tag{3.8}$$

$$A_{23} - A_{32} + A_{34} - A_{43} + A_{42} - A_{24} = 0 \tag{3.9}$$

$$A_{23} - A_{32} + A_{35} - A_{53} + A_{52} - A_{25} = 0 \tag{3.10}$$

$$A_{24} - A_{42} + A_{45} - A_{54} + A_{52} - A_{25} = 0 \tag{3.11}$$

That is only fourteen out of twenty binary interaction parameters are independent.

### 3.2.2 Implementation of Closure equation/s in Parameter Estimation

The closure equation/s have been implemented by the elimination of the parameters, $A_{ij}$'s equal to the number of closure equation/s. These eliminated parameters can be obtained by the simultaneous solution of closure equation/s. There exist several possibilities of parameter elimination for ternary, quaternary and quinary systems. However, a feasible set is such that the rank of the coefficient matrix of the eliminated parameters in the closure equation/s is equal to the number of independent closure equation/s. A general expression for the number of feasible sets of parameter elimination for a $c$ component system with $n$ number of closure equation is given as [1, 4],

$$c^{c-2} \times 2^n \text{ where } n = 0.5 \times c(c-3)+1 \qquad (3.12)$$

The following two rules of thumb must be satisfied to obtain the feasible sets of eliminated parameters [4],

1. Mirror images (i.e., $A_{ij}$ and $A_{ji}$) cannot be eliminated simultaneously.
2. Same component cannot appear as subscript in all the eliminated parameters.

## 3.3 Results and Discussion

Implementation of closure equation/s has been studied on same 65 aromatic extraction systems as listed in Table 2.2 of chapter 2.

There exist several possibilities for parameter elimination. The number of such possibilities for ternary system is 6, for quaternary is 220 and for quinary is 38760. However, all such possibilities are not feasible. The number of feasible sets as discussed in section 3.2.2 is 6 for ternary, 128 for quaternary and 8000 for quinary systems. From parameter elimination for ternary systems, it is observed that most of the cases elimination of parameters with only *i*=nonaromatic-*j*=aromatic, *i*=nonaromatic-*j*=solvent and *i*=solvent-*j*=aromatic combination gives better rmsd values than elimination of other binary pairs. Therefore, for quaternary and quinary systems feasible sets involving parameters with only these pairings, termed as '*likely feasible sets*' have been considered. The number of such likely feasible sets of parameter elimination is 3 for ternary, 8 for quaternary and 21 for quinary systems. Summary of parameter elimination scheme is given in Table 3.1.

Table 3.1 Parameter elimination scheme

| Parameter elimination procedure | System | | |
|---|---|---|---|
| | Ternary | Quaternary | Quinary |
| number of binary interaction parameters $a = 2 \times {}^{c}C_{2}$ | 6 | 12 | 20 |
| number of closure equation/s $n = 0.5 \times c(c-3)+1$ | 1 | 3 | 6 |
| number of parameter elimination possibilities ${}^{a}C_{n}$ | 6 | 220 | 38760 |
| number of feasible sets of parameter elimination $c^{c-2} \times 2^{n}$ | 6 | 128 | 8000 |
| number of likely feasible sets of parameter elimination | 3 | 8 | 21[a] |

[a] nonaromatic-nonaromatic-aromatic-aromatic-solvent system

The rmsd values thus obtained have been compared with those reported in chapter 2 (without closure equation/s) and reported in the literature in terms of percentage gain defined as,

$$gain_{lit}^{wce} = \frac{rmsd_{lit} - rmsd_{wce}}{rmsd_{lit}} \times 100 \tag{3.13}$$

$$gain_{woce}^{wce} = \frac{rmsd_{woce} - rmsd_{wce}}{rmsd_{woce}} \times 100 \tag{3.14}$$

The results of NRTL and UNIQUAC parameter estimation along with the corresponding percentage gain values for the ternary, quaternary and quinary systems are given in Table 3.2-3.7. Comparison of average rmsd's for all the systems are give in Table 3.8. It is seen that the rmsd value corresponding to the parameters with the closure equation/s taken into account is less than that without closure equation/s; approximately 12, 10 and 7 percent better using NRTL model and 12, 18, and 8 percent better using UNIQUAC model, respectively for ternary, quaternary and quinary systems. This clearly means that parameters obtained with the closure equation/s will predict the LLE more accurately than those obtained without closure equation/s. The overall percentage gain is now approximately 44, 33 and 31 percent better using NRTL model, respectively for ternary, quaternary and quinary systems and 30 percent better for ternary systems using UNIQUAC model, than literature values.

Table 3 2 NRTL (α=0.2) binary interaction parameters with closure equation for ternary aromatic extraction systems at different temperatures

| System No. | Temp. (°C) | Binary Interaction Parameters, with closure equation (K) | | | | | | rmsd | $gain^{wce}_{w/oce}$ (%) | $gain^{wce}_{lit}$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $A_{12}$ | $A_{21}$ | $A_{13}$ | $A_{31}$ | $A_{23}$ | $A_{32}$ | | | |
| 1 | 17 | 22.28 | 498.13 | 935.74 | 866.14 | 575.46 | 30.01 | 0.0054 | 15.63 | n.a. |
| | 25 | 62.89 | 150.48 | 1405.30 | 931.50 | 471.17 | -90.22 | 0.0033 | 10.81 | n.a. |
| | 50 | -1.73 | 292.81 | 1208.20 | 1035.10 | 446.78 | -20.86 | 0.0041 | 12.77 | n.a. |
| 2 | 17 | 239.60 | -78.33 | 1385.10 | 707.75 | 421.69 | 62.27 | 0.0052 | -1.96 | n.a. |
| | 25 | 319.31 | -222.13 | 1731.90 | 704.12 | 487.78 | 1.44 | 0.0029 | 29.27 | n.a. |
| | 50 | 56.59 | 28.68 | 1360.30 | 473.37 | 728.12 | -130.90 | 0.0064 | 4.48 | n.a. |
| 3 | 25 | 57.18 | 56.05 | 1533.00 | 897.63 | 489.35 | -144.89 | 0.004 | 20.00 | n.a. |
| | 30 | 1789.10 | 216.20 | 1001.20 | 807.95 | 173.99 | 1553.64 | 0.007 | 0.00 | n.a. |
| | 50 | 242.04 | -108.76 | 1737.40 | 905.99 | 414.67 | -65.94 | 0.003 | 25.00 | n.a. |
| | 75 | 58.19 | -140.41 | 1541.80 | 632.34 | 513.18 | -197.68 | 0.006 | 0.00 | n.a. |
| | 100 | 88.33 | -90.35 | 1541.70 | 663.58 | 518.36 | -181.08 | 0.004 | 0.00 | n.a. |
| 4 | 25 | 62.05 | -49.75 | 1698.50 | 700.64 | 676.44 | -209.62 | 0.003 | 50.00 | 40.00 |
| | 35 | 108.23 | -178.38 | 1812.50 | 709.68 | 801.31 | -14.90 | 0.009 | 0.00 | 43.75 |
| | 50 | -367.42 | -54.75 | 1770.00 | 811.60 | 1073.20 | -197.87 | 0.005 | 0.00 | 66.67 |
| 5 | 25 | 93.98 | 76.29 | 1177.90 | 682.86 | 548.75 | 71.40 | 0.004 | 20.00 | 50.00 |
| | 35 | -259.05 | 21.32 | 1375.90 | 623.33 | 1140.30 | 107.36 | 0.004 | 0.00 | 75.00 |
| | 50 | -41.89 | -179.60 | 1681.80 | 745.66 | 944.19 | 145.76 | 0.002 | 0.00 | 80.00 |
| 6 | 25 | 70.98 | 163.81 | 1629.20 | 1269.20 | 438.29 | -14.54 | 0.0037 | 11.90 | n.a. |
| | 110 | -110.58 | 382.52 | 980.28 | 765.35 | 632.49 | -75.54 | 0.003 | 25.00 | n.a. |
| 7 | 25 | -47.29 | 114.52 | 1301.40 | 902.44 | 535.01 | -25.76 | 0.004 | 20.00 | n.a. |
| | 30 | 1499.80 | -29.95 | 817.79 | 904.63 | -347.83 | 1268.76 | 0.002 | 0.00 | n.a. |
| | 50 | 141.11 | -118.86 | 1602.80 | 861.54 | 482.38 | 1.09 | 0.002 | 0.00 | n.a. |
| | 75 | 249.37 | -174.81 | 1454.90 | 823.17 | 351.69 | 144.14 | 0.003 | 25.00 | n.a. |
| | 100 | -49.67 | -77.92 | 1264.60 | 724.86 | 459.77 | -51.72 | 0.003 | 0.00 | n.a. |
| 8 | 17 | 183.42 | -69.21 | 1449.90 | 1020.30 | 369.26 | 192.29 | 0.011 | 15.38 | n.a. |
| | 25 | 147.51 | -136.49 | 1633.30 | 932.09 | 513.19 | 95.98 | 0.005 | 0.00 | n.a. |
| | 50 | 186.99 | -147.46 | 1487.50 | 852.06 | 446.14 | 145.15 | 0.007 | -16.67 | n.a. |
| 9 | 25 | 50.67 | 890.62 | 942.22 | 963.46 | 886.10 | 67.39 | 0.003 | 40.00 | 50.00 |
| | 35 | 343.33 | 1178.10 | 766.14 | 1191.20 | 868.03 | 458.32 | 0.005 | 16.67 | 44.44 |
| | 45 | 67.73 | 639.72 | 1031.50 | 1259.50 | 551.67 | 207.68 | 0.003 | 25.00 | 40.00 |
| | 50 | -443.27 | 739.45 | 1025.00 | 1130.40 | 810.87 | -266.45 | 0.004 | 20.00 | 33.33 |
| | 75 | -323.95 | 325.02 | 1383.10 | 960.15 | 751.21 | -320.71 | 0.003 | 0.00 | 0.00 |
| | 100 | 14.24 | 203.06 | 1377.40 | 1214.80 | 438.84 | 87.42 | 0.005 | -25.00 | 44.44 |
| 10 | 25 | -290.79 | 556.16 | 899.19 | 1059.00 | 670.37 | -16.77 | 0.002 | 0.00 | 0.00 |
| | 35 | -333.89 | 288.43 | 1034.10 | 1079.70 | 498.44 | -78.28 | 0.002 | 0.00 | 0.00 |
| | 45 | -428.57 | 518.98 | 865.29 | 1016.50 | 672.36 | -123.98 | 0.002 | 0.00 | 33.33 |
| | 50 | -693.18 | 206.43 | 1243.00 | 969.69 | 752.26 | -420.66 | 0.006 | 0.00 | 14.29 |
| | 75 | -195.17 | 153.63 | 1414.80 | 978.95 | 662.36 | -122.29 | 0.003 | 0.00 | 40.00 |
| | 100 | -297.75 | 236.26 | 1311.50 | 910.97 | 773.30 | -161.24 | 0.003 | 0.00 | 25.00 |
| 11 | 25 | -405.38 | 276.52 | 950.11 | 1000.10 | 563.18 | -68.73 | 0.003 | 0.00 | 0.00 |
| | 30 | 327.31 | 392.35 | 804.39 | 958.49 | 344.08 | 433.14 | 0.003 | 0.00 | n.a. |

(continued on next page)

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 35 | -197.41 | 93.50 | 1122.00 | 898.03 | 508.14 | -6.74 | 0.002 | 0.00 | 33.33 |
| | 45 | 37.79 | -71.60 | 1267.90 | 986.91 | 295.91 | 124.31 | 0.003 | 25.00 | 0.00 |
| | 50 | -82.57 | 61.38 | 1462.30 | 1040.80 | 636.53 | 71.08 | 0.002 | 0.00 | 0.00 |
| | 75 | -93.54 | 171.18 | 1362.90 | 1117.80 | 584.36 | 74.54 | 0.003 | 25.00 | 0.00 |
| | 100 | -126.24 | 233.03 | 1160.90 | 1139.00 | 556.37 | 175.20 | 0.003 | 0.00 | 25.00 |
| 12 | 25 | 202.79 | -251.48 | 1892.00 | 577.38 | 564.85 | -295.50 | 0.004 | 0.00 | n.a. |
| | 50 | 418.74 | 107.14 | 1083.00 | 530.96 | 444.85 | 204.41 | 0.007 | -133.33 | n.a. |
| | 75 | 716.38 | -364.43 | 1501.90 | 466.66 | 185.76 | 231.33 | 0.003 | 25.00 | n.a. |
| | 100 | 392.24 | -398.89 | 1347.70 | 384.68 | 209.39 | 37.50 | 0.002 | 50.00 | n.a. |
| 13 | 25 | -30.47 | -175.02 | 1424.10 | 628.66 | 476.79 | -174.10 | 0.009 | -12.50 | 10.00 |
| 14 | 35 | 336.45 | -372.93 | 1892.00 | 537.19 | 775.64 | 130.19 | 0.005 | 0.00 | 50.00 |
| | 50 | 416.73 | -433.65 | 1861.00 | 434.47 | 714.40 | 138.25 | 0.005 | 16.67 | 54.55 |
| 15 | 25 | 50.27 | -141.13 | 1788.30 | 1000.20 | 462.82 | -133.88 | 0.006 | 14.29 | 57.14 |
| 16 | 25 | 107.15 | -219.85 | 1547.10 | 507.42 | 467.14 | -245.54 | 0.003 | 0.00 | n.a. |
| | 50 | 131.44 | -67.38 | 1206.10 | 479.31 | 435.41 | -92.56 | 0.003 | 25.00 | n.a. |
| | 75 | 117.60 | -6.84 | 1119.90 | 439.69 | 478.30 | -77.47 | 0.003 | 25.00 | n.a. |
| | 100 | 482.49 | 107.42 | 1004.00 | 456.13 | 466.68 | 293.88 | 0.003 | 25.00 | n.a. |
| 17 | 25 | 309.79 | -145.39 | 1364.00 | 797.12 | 296.77 | 185.07 | 0.005 | 28.57 | 50.00 |
| 18 | 25 | 436.47 | -330.99 | 1517.40 | 664.24 | 199.38 | 113.68 | 0.005 | 0.00 | 28.57 |
| 19 | 25 | 448.74 | -356.04 | 1546.60 | 636.61 | 276.61 | 171.40 | 0.003 | 25.00 | 50.00 |
| 20 | 10 | -246.88 | 341.93 | 1376.80 | 664.95 | 970.50 | -330.16 | 0.0038 | 20.83 | n.a. |
| | 25 | -91.31 | 184.83 | 1187.90 | 717.28 | 557.23 | -189.53 | 0.0040 | 36.51 | n.a. |
| | 50 | -119.17 | 315.04 | 913.56 | 704.71 | 529.90 | -113.16 | 0.0032 | 8.57 | n.a. |
| 21 | 20.5 | 63.12 | -28.52 | 1337.40 | 718.56 | 440.82 | -86.38 | 0.0036 | 21.74 | n.a. |
| 22 | 25 | -166.26 | 333.38 | 858.68 | 807.70 | 585.40 | 34.78 | 0.0044 | 33.33 | n.a. |
| 23 | 20 | 623.30 | -446.51 | 1538.10 | 494.30 | 196.18 | 222.19 | 0.0022 | 12.00 | n.a. |
| 24 | 20 | 281.19 | 680.42 | 773.29 | 1009.50 | 960.05 | 797.03 | 0.0051 | -8.51 | n.a. |
| | 30 | -262.16 | 660.95 | 578.19 | 1288.60 | 929.70 | 717.00 | 0.0046 | 2.13 | n.a. |
| | 40 | -323.46 | 839.18 | 475.83 | 1094.70 | 1295.70 | 751.93 | 0.0031 | -6.90 | n.a. |
| | 50 | -114.77 | 915.37 | 416.51 | 921.70 | 1272.90 | 747.95 | 0.0123 | -39.77 | n.a. |
| 25 | 50 | -199.68 | 503.59 | 1520.50 | 1462.10 | 793.44 | 31.77 | 0.0055 | 3.51 | n.a. |
| 26 | 25 | -360.95 | 475.02 | 1589.40 | 708.37 | 1808.70 | 91.70 | 0.0018 | 10.00 | n.a. |
| 27 | 20 | -291.05 | 470.90 | 1488.80 | 643.41 | 1341.00 | -266.34 | 0.0036 | 7.69 | n.a. |
| 28 | 20 | -391.02 | 519.30 | 1614.00 | 746.51 | 1467.90 | -309.91 | 0.0026 | 27.78 | n.a. |
| 29 | 25 | -77.16 | 304.67 | 1794.00 | 734.69 | 1344.40 | -96.74 | 0.0016 | 5.88 | n.a. |
| 30 | 20 | -452.76 | 636.36 | 1077.20 | 430.65 | 1443.50 | -292.17 | 0.0066 | -10.00 | n.a. |
| 31 | 29 | 110.34 | 1327.00 | 164.05 | 1652.00 | 399.13 | 670.42 | 0.0062 | 1.59 | n.a. |
| | 45 | -183.60 | 1002.10 | 307.52 | 1432.80 | 411.47 | 351.05 | 0.0100 | 0.99 | n.a. |
| | 54.5 | -78.02 | 344.74 | 778.09 | 1629.90 | 41.22 | 470.27 | 0.0025 | 24.24 | n.a. |
| 32 | 25.5 | 42.93 | 1470.20 | 444.47 | 1763.80 | 702.17 | 594.23 | 0.0040 | 0.00 | n.a. |
| | 39 | -380.83 | -77.20 | 920.45 | 1107.00 | 376.52 | 259.44 | 0.0073 | -2.82 | n.a. |
| | 50 | -42.72 | 183.44 | 903.79 | 1342.90 | 254.08 | 467.03 | 0.0081 | 2.41 | n.a. |
| 33 | 50 | -351.40 | 716.79 | 1169.30 | 889.92 | 1416.40 | 68.83 | 0.0027 | 15.63 | n.a. |
| 34 | 50 | -164.18 | 202.48 | 1673.30 | 946.85 | 1277.60 | 184.49 | 0.0020 | 0.00 | n.a. |
| 35 | 25 | 993.84 | 367.94 | 553.20 | 323.99 | 477.15 | 873.84 | 0.0027 | 6.90 | 64.94 |
| 36 | 25 | 501.94 | -142.09 | 492.24 | 463.51 | -177.53 | 437.77 | 0.0011 | 47.62 | n.a. |
| | *(continued on next page)* | | | | | | | | | |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 37 | 15 | 1500.00 | -104.59 | 564.52 | 406.79 | -30.67 | 1416.19 | 0.002 | 50.00 | 50.00 |
| | 25 | 1088.60 | -210.32 | 483.67 | 431.10 | -195.17 | 1051.18 | 0.001 | 50.00 | 75.00 |
| | 40 | 1890.40 | 144.86 | 389.69 | 407.04 | 141.23 | 1904.12 | 0.001 | 50.00 | 92.86 |
| 38 | 20 | 98.39 | -76.12 | 1613.90 | 490.35 | 809.46 | -139.58 | 0.0041 | 30.51 | n.a. |
| | 25 | 114.65 | -174.98 | 1749.30 | 478.28 | 800.18 | -181.21 | 0.0013 | 50.00 | 86.46 |
| 39 | 20 | -122.90 | -43.56 | 1683.40 | 486.90 | 1007.10 | -268.74 | 0.0042 | -121.05 | n.a. |
| 40 | 25 | -116.55 | 75.85 | 1246.50 | 456.00 | 803.99 | -178.91 | 0.0017 | 52.78 | 75.71 |
| 41 | 20 | 222.93 | 76.90 | 566.74 | 511.82 | 117.83 | 208.94 | 0.0011 | 8.33 | n.a. |
| 42 | 20 | 1778.50 | 979.88 | 491.37 | 949.08 | 630.24 | 1886.57 | 0.0028 | 12.5 | n.a. |
| | 30 | 585.55 | 1811.60 | 405.65 | 962.18 | 1337.80 | 668.28 | 0.0030 | 31.82 | n.a. |
| | 40 | 1368.60 | -618.35 | 477.94 | 1007.20 | -762.94 | 1753.27 | 0.0073 | 13.10 | n.a. |
| 43 | 20 | 701.95 | 672.74 | 401.32 | 827.94 | 359.28 | 815.11 | 0.0101 | -31.17 | n.a. |
| | 30 | -578.40 | -674.22 | 1282.80 | 941.34 | -219.37 | -465.01 | 0.0068 | 2.86 | n.a. |
| | 40 | 52.32 | 602.59 | 337.26 | 1105.60 | 259.32 | 477.39 | 0.0076 | 5.00 | n.a. |
| | 50 | 477.13 | 589.80 | 323.41 | 1037.90 | 216.47 | 818.29 | 0.0027 | 52.63 | n.a. |
| 44 | 40 | -737.16 | 308.24 | 1403.90 | 1508.60 | 896.18 | -44.52 | 0.0022 | 0.00 | n.a. |
| | 45 | -194.49 | 324.52 | 1341.10 | 1641.20 | 639.87 | 420.96 | 0.0009 | 10.00 | n.a. |
| | 50 | 187.74 | -119.95 | 1638.90 | 1501.80 | 347.73 | 518.32 | 0.0005 | 37.5 | n.a. |
| | 55 | -586.47 | -417.74 | 1641.60 | 1333.70 | 447.48 | -29.15 | 0.0047 | -6.82 | n.a. |
| | 60 | -823.21 | -66.610 | 1408.80 | 1353.90 | 705.96 | -105.54 | 0.0011 | 15.38 | n.a. |
| 45 | 25 | 103.23 | -114.70 | 1599.20 | 607.62 | 677.82 | -95.83 | 0.0012 | 55.56 | n.a. |
| 46 | 25 | -114.52 | 7.83 | 1579.00 | 650.22 | 912.91 | -138.22 | 0.0019 | 13.64 | n.a. |
| 47 | 25 | -547.99 | -625.79 | 576.03 | 344.72 | -432.25 | -585.76 | 0.0019 | 26.92 | n.a. |
| 48 | 25 | 75.81 | 87.45 | 1162.80 | 514.26 | 557.32 | -102.86 | 0.0026 | 48.00 | n.a. |
| 49 | 25 | 407.25 | -111.22 | 1163.70 | 653.49 | 328.48 | 336.74 | 0.0039 | -5.41 | n.a. |
| 50 | 25 | 788.83 | 27.08 | 737.06 | 529.40 | 108.25 | 662.34 | 0.002 | 33.33 | 0.00 |
| 51 | 25 | 526.59 | -55.56 | 629.62 | 571.32 | 5.75 | 529.60 | 0.001 | 75.00 | 66.67 |
| 52 | 25 | -6.94 | -310.81 | 755.24 | 385.34 | 111.96 | 45.93 | 0.001 | 50.00 | 50.00 |
| 53 | 25 | 78.27 | 64.56 | 683.76 | 292.64 | 340.86 | -36.55 | 0.002 | 50.00 | n.a. |
| **average rmsd** | | | | | | | | **0.0038** | **11.63** | **44.12** |

n.a.: not available/not applicable

Table 3.3 NRTL (α=0.2) binary interaction parameters with closure equations for quaternary aromatic extraction systems at 25°C (r=40°C)

| System No. | Binary Interaction Parameters, with closure equations (K) | | | | | | rmsd | $gain^{wce}_{woce}$ (%) | $gain^{wce}_{lit}$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| | $A_{12}$ | $A_{13}$ | $A_{14}$ | $A_{23}$ | $A_{24}$ | $A_{34}$ | | | |
| | $A_{21}$ | $A_{31}$ | $A_{41}$ | $A_{32}$ | $A_{42}$ | $A_{43}$ | | | |
| 54 | 169.21 | -58.86 | 1028.33 | 165.14 | 317.52 | 697.07 | 0.005 | 16.67 | 28.57 |
| | 213.36 | 417.49 | 990.17 | 597.34 | 235.21 | 182.56 | | | |
| 55 | 423.65 | -45.49 | 1126.24 | 231.54 | 421.79 | 505.43 | 0.005 | 0.00 | 16.67 |
| | 317.42 | 253.14 | 1003.10 | 636.40 | 404.88 | 83.66 | | | |
| 56 | -372.04 | -111.71 | 666.49 | 1058.30 | 1667.70 | 427.96 | 0.006 | -20.00 | 14.29 |
| | 1691.50 | 410.51 | 999.27 | -483.02 | -63.06 | 238.52 | | | |

(*continued on next page*)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 57 | 398.05 | 300.88 | 1754.91 | -107.64 | 882.65 | 453.28 | 0.004 | 0.00 | 20.00 |
| | -408.55 | -112.34 | 972.00 | 285.74 | 906.34 | 83.59 | | | |
| 58 | 381.45 | 1715.20 | 827.56 | 1305.50 | 911.29 | 507.05 | 0.006 | 0.00 | 40.00 |
| | 35.34 | 890.35 | 794.46 | 826.76 | 1224.30 | 1298.80 | | | |
| 59 | -90.27 | -106.64 | 974.01 | -324.17 | 942.71 | 691.39 | 0.004 | 0.00 | 42.86 |
| | -95.63 | 337.23 | 727.41 | 125.06 | 701.47 | 0.92 | | | |
| 60 | 1562.30 | 222.46 | 1755.28 | 128.93 | 1110.30 | 321.96 | 0.003 | 25.00 | 25.00 |
| | 936.28 | -176.86 | 951.43 | 355.63 | 932.47 | -82.57 | | | |
| 61 | 694.62 | 1655.24 | 987.72 | 226.10 | 1832.00 | 253.05 | 0.003 | 40.00 | 66.67 |
| | 1456.20 | 1559.40 | 1044.00 | -631.32 | 1126.70 | 405.17 | | | |
| 62 | 1049.40 | 924.07 | 501.98 | 1248.70 | 505.32 | -158.17 | 0.007 | -16.67 | n.a. |
| | 511.13 | 266.20 | 425.58 | 1129.10 | 967.19 | 423.30 | | | |
| $62^r$ | 1078.70 | 833.88 | 273.48 | 1502.70 | 1726.90 | -928.43 | 0.003 | -50.00 | n.a. |
| | 1610.60 | -232.40 | 475.68 | -95.48 | 1397.20 | 340.05 | | | |
| **average rmsd** | | | | | | | **0.0046** | **9.80** | **33.33** |

n.a.: not available/not applicable

Table 3.4 NRTL (α=0.2) binary interaction parameters with closure equations for quinary aromatic extraction systems at 25 °C

| **System No.** | **Binary Interaction Parameters, with closure equations (K)** | | | | | **rmsd** | $gain_{woce}^{wce}$ **(%)** | $gain_{lit}^{wce}$ **(%)** |
|---|---|---|---|---|---|---|---|---|
| | $A_{12}$ | $A_{21}$ | $A_{31}$ | $A_{41}$ | $A_{51}$ | | | |
| | $A_{13}$ | $A_{23}$ | $A_{32}$ | $A_{42}$ | $A_{52}$ | | | |
| | $A_{14}$ | $A_{24}$ | $A_{34}$ | $A_{43}$ | $A_{53}$ | | | |
| | $A_{15}$ | $A_{25}$ | $A_{35}$ | $A_{45}$ | $A_{54}$ | | | |
| 63 | -78.52 | 1207.7 | 670.73 | 1272.6 | 1221.9 | 0.006 | 14.29 | 33.33 |
| | 2.64 | 544.27 | -73.86 | 323.46 | 1128 | | | |
| | -754.05 | -416.97 | -251.37 | 1107.19 | 386.08 | | | |
| | 507.88 | 1700.2 | 340.15 | 1125.4 | -187.23 | | | |
| 64 | -15.19 | 85.65 | 313.07 | 167.42 | 764.89 | 0.006 | -20.00 | -50.00 |
| | 58.01 | 107.35 | 261.57 | 144.29 | 1111.1 | | | |
| | -66.33 | 11.38 | 626.78 | 605.47 | 52.35 | | | |
| | 1023.05 | 1470.1 | 565.57 | 520.89 | 28.98 | | | |
| 65 | 1574.5 | 1481.5 | 569.01 | 226.59 | 1503.1 | 0.004 | 20.00 | 60.00 |
| | 95.27 | 152.54 | 719.28 | 571.54 | 1527.7 | | | |
| | -574.04 | -322.09 | -212.54 | 114.35 | 208.14 | | | |
| | 1187.9 | 1119.5 | 366.68 | 395.01 | -90.42 | | | |
| **average rmsd** | | | | | | **0.0053** | **7.02** | **31.17** |

Table 3 5 UNIQUAC binary interaction parameters with closure equation for ternary aromatic extraction systems at different temperatures

| System No. | Temp. (°C) | Binary Interaction Parameters, with closure equation (K) | | | | | | rmsd | $gain^{wce}_{woce}$ (%) | $gain^{wce}_{lit}$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $A_{12}$ | $A_{21}$ | $A_{13}$ | $A_{31}$ | $A_{23}$ | $A_{32}$ | | | |
| 1 | 17 | 319.87 | -16.19 | 311.90 | 285.91 | 5.29 | 315.36 | 0.0065 | 30.11 | n.a. |
| | 25 | 42.07 | 101.41 | 257.42 | 241.49 | 134.94 | 59.67 | 0.0045 | 23.73 | n.a. |
| | 50 | -14.37 | -22.37 | 456.24 | 146.03 | 187.82 | -114.39 | 0.0048 | 11.11 | n.a. |
| 2 | 17 | 309.35 | -174.20 | 618.56 | 123.38 | 75.36 | 63.73 | 0.0057 | 18.57 | n.a. |
| | 25 | 105.54 | -101.67 | 515.34 | 86.98 | 187.13 | -34.02 | 0.0043 | -22.86 | n.a. |
| | 50 | 406.48 | -214.90 | 670.58 | 198.82 | 21.72 | 171.34 | 0.0085 | -25.00 | n.a. |
| 3 | 25 | 299.75 | -81.21 | 367.10 | 182.57 | 16.75 | 213.18 | 0.006 | 0.00 | n.a. |
| | 30 | 905.56 | -50.68 | 367.13 | 99.55 | 13.16 | 701.82 | 0.007 | 22.22 | n.a. |
| | 50 | 463.66 | -268.49 | 690.30 | 112.75 | -36.17 | 118.43 | 0.004 | 20.00 | n.a. |
| | 75 | 288.04 | -243.42 | 661.99 | 13.07 | 95.27 | -22.19 | 0.007 | 12.50 | n.a. |
| | 100 | 362.39 | -101.39 | 393.99 | 113.41 | 49.70 | 232.90 | 0.008 | -33.33 | n.a. |
| 4 | 25 | 241.62 | -151.67 | 637.25 | 73.91 | 152.60 | -17.45 | 0.003 | 40.00 | n.a. |
| | 35 | 301.77 | -210.31 | 697.68 | 60.41 | 165.66 | 40.47 | 0.010 | 0.00 | 50.00 |
| | 50 | -328.17 | 153.53 | 517.67 | 61.70 | 697.79 | -239.88 | 0.005 | 0.00 | 54.55 |
| 5 | 25 | 459.01 | -221.61 | 954.65 | 53.75 | 196.31 | -23.97 | 0.004 | 42.86 | n.a. |
| | 35 | -191.48 | 158.71 | 353.69 | 98.75 | 530.05 | -75.08 | 0.004 | 0.00 | 66.67 |
| | 50 | -10.72 | -74.13 | 531.68 | 76.47 | 360.05 | -31.75 | 0.002 | 50.00 | 88.89 |
| 6 | 25 | 414.62 | -240.71 | 744.69 | 170.01 | -7.01 | 73.64 | 0.0045 | 11.76 | n.a. |
| | 110 | 421.53 | -146.68 | 405.71 | 78.50 | 14.89 | 255.89 | 0.005 | 37.50 | n.a. |
| 7 | 25 | 220.44 | -64.39 | 357.18 | 234.87 | 28.47 | 190.99 | 0.009 | 0.00 | n.a. |
| | 30 | 702.28 | -152.71 | 311.33 | 117.66 | -155.37 | 505.95 | 0.002 | 0.00 | n.a. |
| | 50 | 111.49 | -106.09 | 479.87 | 51.00 | 182.02 | -29.27 | 0.003 | 25.00 | n.a. |
| | 75 | 308.47 | -233.72 | 650.05 | 11.46 | 113.05 | 16.65 | 0.002 | 33.33 | n.a. |
| | 100 | 426.60 | -264.65 | 570.18 | 40.27 | -5.56 | 155.78 | 0.004 | 0.00 | n.a. |
| 8 | 17 | 154.85 | -105.64 | 467.75 | 102.42 | 133.97 | 29.13 | 0.011 | -22.22 | n.a. |
| | 25 | -75.08 | 19.77 | 376.15 | 78.09 | 304.20 | -88.71 | 0.007 | 12.50 | n.a. |
| | 50 | 8.32 | -2.83 | 336.65 | 136.19 | 186.98 | -2.33 | 0.009 | -12.50 | n.a. |
| 9 | 25 | 522.15 | -49.81 | 415.12 | 114.80 | 91.31 | 362.95 | 0.003 | 25.00 | 25.00 |
| | 35 | 386.10 | -12.71 | 336.19 | 200.29 | 69.69 | 332.60 | 0.005 | 50.00 | 44.44 |
| | 45 | 203.31 | -112.49 | 528.51 | 61.14 | 144.60 | -6.97 | 0.004 | 33.33 | 33.33 |
| | 50 | 812.96 | 9.57 | 332.88 | 254.33 | 49.51 | 774.35 | 0.007 | 12.50 | -40.00 |
| | 75 | 328.53 | -29.77 | 334.04 | 187.61 | 71.73 | 283.60 | 0.008 | -166.67 | -100.00 |
| | 100 | 441.07 | -228.79 | 529.93 | 110.82 | -29.69 | 221.06 | 0.006 | 0.00 | 25.00 |
| 10 | 25 | -217.18 | 611.49 | 304.55 | 101.08 | 899.71 | -132.43 | 0.005 | 28.57 | -150.00 |
| | 35 | -322.67 | 95.13 | 372.99 | 73.46 | 400.39 | -316.94 | 0.005 | 0.00 | -66.67 |
| | 45 | 533.30 | -295.27 | 667.01 | 90.06 | -65.82 | 185.80 | 0.006 | 25.00 | -100.00 |
| | 50 | 300.64 | -237.15 | 706.43 | 135.17 | 79.52 | 46.05 | 0.006 | 14.29 | 14.29 |
| | 75 | -65.16 | 1.26 | 461.96 | 48.13 | 336.30 | -143.95 | 0.004 | 0.00 | 20.00 |
| | 100 | -289.42 | 211.55 | 443.27 | 38.00 | 623.09 | -283.15 | 0.006 | -100.00 | -20.00 |
| 11 | 25 | -141.76 | 114.61 | 232.99 | 263.61 | 182.74 | -43.01 | 0.006 | 14.29 | -50.00 |
| | 30 | 127.64 | 317.93 | 197.47 | 223.97 | 334.58 | 170.79 | 0.008 | 11.11 | n.a. |

*(continued on next page)*

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|---|---|---|---|---|---|---|---|---|---|---|
| | 35 | -222.17 | 232.77 | 255.01 | 139.22 | 413.57 | -157.16 | 0.008 | 0.00 | -100.00 |
| | 45 | -34.69 | -29.11 | 412.92 | 46.23 | 258.94 | -113.33 | 0.004 | 33.33 | 20.00 |
| | 50 | -189.22 | 206.87 | 374.46 | 89.48 | 533.62 | -147.45 | 0.005 | 28.57 | 16.67 |
| | 75 | -239.85 | 270.71 | 330.30 | 108.75 | 541.72 | -190.39 | 0.007 | 12.50 | -75.00 |
| | 100 | 154.39 | -93.62 | 436.78 | 160.32 | 117.82 | 89.37 | 0.005 | -66.67 | -66.67 |
| 12 | 25 | 51.34 | -35.42 | 359.73 | 105.84 | 131.85 | -35.28 | 0.005 | 16.67 | n.a. |
| | 50 | 232.91 | -48.79 | 357.08 | 108.52 | 87.33 | 120.47 | 0.008 | -60.00 | n.a. |
| | 75 | 730.89 | -333.79 | 670.77 | 49.95 | -145.16 | 298.70 | 0.006 | 14.29 | n.a. |
| | 100 | 293.99 | -313.01 | 551.58 | 21.09 | -43.00 | 33.51 | 0.003 | 25.00 | n.a. |
| 13 | 25 | 940.22 | 143.73 | 468.68 | 157.30 | 29.74 | 514.85 | 0.007 | 12.50 | n.a. |
| 14 | 35 | 290.88 | -220.03 | 873.22 | 43.62 | 296.92 | -21.76 | 0.005 | 16.67 | 54.55 |
| | 50 | 380.39 | -257.82 | 935.42 | 12.56 | 270.38 | -14.27 | 0.005 | 16.67 | 68.75 |
| 15 | 25 | 208.69 | -119.54 | 443.69 | 196.05 | 31.45 | 112.04 | 0.008 | 11.11 | n.a. |
| 16 | 25 | 225.42 | -191.02 | 508.71 | 35.69 | 58.87 | 2.29 | 0.003 | 40.00 | n.a. |
| | 50 | 401.38 | -196.08 | 439.29 | 58.82 | -24.46 | 192.53 | 0.005 | 28.57 | n.a. |
| | 75 | 537.89 | -178.78 | 395.61 | 60.43 | -43.33 | 338.16 | 0.006 | -50.00 | n.a. |
| | 100 | 379.82 | -203.92 | 441.44 | 18.19 | 7.26 | 167.75 | 0.004 | 20.00 | n.a. |
| 17 | 25 | 278.07 | -159.23 | 460.72 | 135.38 | 21.22 | 133.18 | 0.006 | 14.29 | n.a. |
| 18 | 25 | 435.57 | -315.91 | 889.45 | -27.72 | 95.12 | -70.57 | 0.007 | 22.22 | n.a. |
| 19 | 25 | 569.50 | -296.72 | 856.38 | -6.35 | 55.43 | 58.92 | 0.005 | 44.44 | n.a. |
| 20 | 10 | 127.64 | -13.75 | 507.34 | 119.00 | 238.97 | -7.98 | 0.0056 | 40.43 | n.a. |
| | 25 | 225.50 | -184.55 | 974.00 | 49.00 | 337.29 | -177.66 | 0.0038 | 0.00 | n.a. |
| | 50 | 356.98 | -164.27 | 578.78 | 90.10 | 63.93 | 96.50 | 0.0044 | -46.67 | n.a. |
| 21 | 20.5 | 249.94 | -144.32 | 556.36 | 78.82 | 110.98 | 27.70 | 0.0064 | 17.95 | n.a. |
| 22 | 25 | 5.89 | 9.21 | 498.89 | 57.27 | 361.11 | -83.83 | 0.0044 | 10.20 | n.a. |
| 23 | 20 | 293.47 | -179.52 | 605.46 | 73.24 | 109.14 | 49.91 | 0.0042 | -7.69 | n.a. |
| 24 | 20 | 84.88 | 146.50 | 495.96 | 119.89 | 551.72 | 114.03 | 0.0048 | 5.88 | n.a. |
| | 30 | -118.39 | 222.34 | 364.45 | 225.71 | 560.90 | 81.43 | 0.0047 | 0.00 | n.a. |
| | 40 | -167.55 | 308.37 | 372.49 | 129.29 | 794.16 | 75.04 | 0.0033 | 8.33 | n.a. |
| | 50 | -129.62 | 350.45 | 371.25 | 80.47 | 836.94 | 66.09 | 0.0126 | -28.57 | n.a. |
| 25 | 50 | -74.13 | 146.31 | 221.93 | 294.97 | 190.58 | 43.18 | 0.0061 | 17.57 | n.a. |
| 26 | 25 | -125.22 | 151.41 | 457.13 | 50.15 | 614.26 | -69.35 | 0.0018 | 10.00 | n.a. |
| 27 | 20 | 23.42 | 18.77 | 364.02 | 93.20 | 239.52 | -26.65 | 0.0029 | 60.81 | n.a. |
| 28 | 20 | 165.80 | -95.55 | 493.93 | 60.19 | 179.18 | 6.79 | 0.0021 | 32.26 | n.a. |
| 29 | 25 | -189.75 | 416.73 | 408.72 | 44.14 | 836.87 | -134.19 | 0.0045 | 28.57 | n.a. |
| 30 | 20 | -181.72 | 247.85 | 390.95 | 52.39 | 613.70 | -154.43 | 0.0074 | 5.13 | n.a. |
| 31 | 29 | -292.60 | 504.47 | -112.30 | 404.61 | 211.46 | -68.70 | 0.0068 | 21.84 | n.a. |
| | 45 | 31.04 | 302.10 | -142.80 | 605.15 | -53.81 | 423.08 | 0.0119 | -16.67 | n.a. |
| | 54.5 | -34.83 | -9.83 | 2.42 | 259.09 | -62.20 | 169.47 | 0.0085 | -34.92 | n.a. |
| 32 | 25.5 | -14.87 | 322.58 | -95.56 | 600.55 | -27.97 | 330.69 | 0.0042 | 31.15 | n.a. |
| | 39 | -50.64 | -90.25 | 14.25 | 302.79 | -90.00 | 238.15 | 0.0089 | -1.14 | n.a. |
| | 50 | 88.16 | -35.18 | -16.26 | 381.14 | -141.00 | 379.74 | 0.0098 | 9.26 | n.a. |
| 33 | 50 | -201.27 | 518.31 | 201.50 | 195.73 | 719.29 | -6.06 | 0.0035 | 7.89 | n.a. |
| 34 | 50 | 67.62 | -63.50 | 508.68 | 92.56 | 325.53 | 40.53 | 0.0021 | 4.55 | n.a. |
| 35 | 25 | 402.53 | 12.81 | 229.64 | 19.17 | 121.81 | 301.06 | 0.0028 | 20.00 | 53.33 |
| 36 | 25 | -270.13 | -249.12 | 189.28 | 61.48 | -246.63 | -395.44 | 0.0045 | 34.78 | n.a. |
| | *(continued on next page)* | | | | | | | | | |

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|---|---|---|---|---|---|---|---|---|---|---|
| 37 | 15 | 676.91 | -170.08 | 255.68 | 13.27 | -83.86 | 520.72 | 0.002 | 75.00 | 50.00 |
| | 25 | 577.84 | -162.56 | 223.40 | 19.77 | -84.55 | 452.22 | 0.002 | 71.43 | 50.00 |
| | 40 | -323.12 | -37.84 | 206.78 | 9.41 | 46.04 | -436.61 | 0.002 | 33.33 | 85.71 |
| 38 | 20 | -122.99 | 217.02 | 524.52 | 35.54 | 691.14 | -137.85 | 0.0076 | -72.73 | n.a. |
| | 25 | 179.48 | -138.68 | 819.03 | 19.96 | 387.11 | -93.80 | 0.0031 | 18.42 | 75.00 |
| 39 | 20 | 29.39 | -76.27 | 932.09 | -30.03 | 673.43 | -183.03 | 0.0050 | -100.00 | n.a. |
| 40 | 25 | 111.00 | -81.27 | 535.74 | 28.44 | 267.67 | -47.36 | 0.0033 | 44.07 | 52.86 |
| 41 | 20 | 301.17 | -137.39 | 338.43 | 12.34 | -3.60 | 108.87 | 0.0013 | 65.79 | n.a. |
| 42 | 20 | 682.61 | 233.79 | 402.59 | -10.42 | 575.06 | 610.87 | 0.0030 | 53.85 | n.a. |
| | 30 | -149.33 | 349.98 | 399.61 | -20.11 | 694.54 | -224.49 | 0.0033 | 46.77 | n.a. |
| | 40 | 922.88 | -502.29 | 419.53 | -4.45 | -445.78 | 555.41 | 0.0071 | 22.83 | n.a. |
| 43 | 20 | 291.15 | -14.90 | 299.88 | 39.50 | 149.76 | 195.43 | 0.0119 | -41.67 | n.a. |
| | 30 | 145.27 | -354.74 | 739.53 | -36.37 | 7.74 | -268.15 | 0.0075 | 20.21 | n.a. |
| | 40 | 112.18 | 76.97 | 257.41 | 82.86 | 218.03 | 78.69 | 0.0110 | -18.28 | n.a. |
| | 50 | 343.47 | -85.80 | 379.22 | -6.50 | 114.93 | 158.48 | 0.0051 | 36.25 | n.a. |
| 44 | 40 | -106.85 | -11.58 | 856.50 | 259.40 | 600.86 | -91.51 | 0.0022 | 8.33 | n.a. |
| | 45 | -44.07 | 74.60 | 754.06 | 459.33 | 443.93 | 30.53 | 0.0011 | 63.33 | n.a. |
| | 50 | -56.87 | 48.54 | 800.03 | 732.39 | 246.09 | 73.04 | 0.0011 | 52.17 | n.a. |
| | 55 | -124.52 | -157.76 | 855.83 | 187.39 | 483.76 | -151.44 | 0.0047 | -9.30 | n.a. |
| | 60 | -100.43 | -110.92 | 883.41 | 294.00 | 481.25 | -97.67 | 0.0009 | 10.00 | n.a. |
| 45 | 25 | 56.36 | -82.14 | 797.65 | -19.69 | 527.16 | -151.68 | 0.0028 | 30.00 | n.a. |
| 46 | 25 | -208.67 | 217.76 | 585.50 | 24.58 | 794.49 | -192.86 | 0.0045 | -50.00 | n.a. |
| 47 | 25 | -104.72 | -278.86 | 297.15 | -37.97 | -126.45 | -287.43 | 0.0035 | 36.36 | n.a. |
| 48 | 25 | -128.37 | 725.69 | 215.30 | 45.63 | 925.42 | -98.31 | 0.0089 | 7.29 | n.a. |
| 49 | 25 | 334.73 | -178.31 | 670.65 | 17.03 | 180.72 | 40.14 | 0.0040 | 51.22 | n.a. |
| 50 | 25 | 892.49 | -244.22 | 492.94 | 69.11 | -156.12 | 556.76 | 0.005 | 28.57 | 37.50 |
| 51 | 25 | 423.57 | -181.82 | 403.81 | 53.77 | -37.06 | 218.29 | 0.003 | 57.14 | 62.50 |
| 52 | 25 | 320.85 | -265.98 | 622.31 | -29.41 | 68.92 | 4.03 | 0.003 | 25.00 | 57.14 |
| 53 | 25 | -756.69 | -41.63 | 339.51 | 26.17 | 168.08 | -860.32 | 0.0038 | 11.63 | n.a. |
| **average rmsd** | | | | | | | | **0.0052** | **11.86** | **29.73** |

n.a.: not available/not applicable

Table 3.6 UNIQUAC binary interaction parameters with closure equations for quaternary aromatic extraction systems at 25°C (r=40°C)

| System No. | Binary Interaction Parameters, with closure equations (K) | | | | | | rmsd | $gain_{woce}^{wce}$ (%) |
|---|---|---|---|---|---|---|---|---|
| | $A_{12}$ | $A_{13}$ | $A_{14}$ | $A_{23}$ | $A_{24}$ | $A_{34}$ | | |
| | $A_{21}$ | $A_{31}$ | $A_{41}$ | $A_{32}$ | $A_{42}$ | $A_{43}$ | | |
| 54 | 442.34 | 561.30 | 1417.95 | 67.00 | 445.77 | 374.94 | 0.008 | 27.27 |
| | -272.93 | -313.08 | 37.44 | -92.11 | -219.47 | -131.19 | | |
| 55 | 331.94 | -108.90 | 304.76 | -322.27 | 50.19 | 279.60 | 0.008 | -14.29 |
| | -26.62 | 106.45 | 138.00 | 251.64 | 241.99 | -102.51 | | |
| 56 | -378.95 | -120.68 | 166.08 | 29.750 | 203.18 | 258.27 | 0.009 | -12.5 |
| | 217.03 | 292.20 | 332.30 | -153.35 | -226.58 | 11.61 | | |

(*continued on next page*)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 57 | -159.40 | -62.05 | 541.02 | 63.82 | 744.02 | 409.92 | 0.009 | 0.00 |
| | 110.54 | -5.67 | 18.20 | -149.74 | -48.74 | -169.28 | | |
| 58 | -297.77 | 905.79 | 455.40 | 1178.50 | 747.86 | 18.70 | 0.007 | 22.22 |
| | 68.65 | -68.02 | 51.32 | -161.73 | -22.64 | 588.43 | | |
| 59 | -584.52 | -3.01 | 337.46 | 32.49 | 481.34 | 205.66 | 0.005 | 28.57 |
| | -412.51 | -289.26 | -176.54 | -425.77 | -204.67 | -22.09 | | |
| 60 | -109.07 | 367.92 | 683.13 | 248.22 | 419.32 | -7.99 | 0.003 | 62.50 |
| | -769.98 | -854.59 | -470.84 | -313.38 | -73.74 | 60.55 | | |
| 61 | 59.15 | 374.83 | 822.42 | 595.37 | 752.14 | 61.62 | 0.005 | 37.50 |
| | -165.07 | -537.65 | -80.92 | -92.89 | 73.02 | 70.76 | | |
| 62 | 330.10 | 800.34 | 331.17 | 363.21 | 297.55 | 249.91 | 0.005 | 16.67 |
| | 10.77 | 225.77 | -57.83 | 107.97 | 227.88 | 435.48 | | |
| $62^r$ | 836.96 | 812.09 | -409.48 | -341.99 | 269.19 | -177.86 | 0.006 | 0.00 |
| | -145.33 | 320.97 | -912.76 | 149.18 | 748.20 | -190.02 | | |
| **average rmsd** | | | | | | | **0.0065** | **17.72** |

Table 3.7 UNIQUAC binary interaction parameters with closure equations for quinary aromatic extraction systems at 25 °C

| **System No.** | **Binary Interaction Parameters, with closure equations (K)** | | | | | **rmsd** | $gain^{wce}_{woce}$ **(%)** |
|---|---|---|---|---|---|---|---|
| | $A_{12}$ | $A_{21}$ | $A_{31}$ | $A_{41}$ | $A_{51}$ | | |
| | $A_{13}$ | $A_{23}$ | $A_{32}$ | $A_{42}$ | $A_{52}$ | | |
| | $A_{14}$ | $A_{24}$ | $A_{34}$ | $A_{43}$ | $A_{53}$ | | |
| | $A_{15}$ | $A_{25}$ | $A_{35}$ | $A_{45}$ | $A_{54}$ | | |
| 63 | -566.03 | -533.46 | 849.10 | 30.10 | 474.46 | 0.015 | 21.05 |
| | 160.56 | -48.67 | 607.30 | 20.11 | 853.39 | | |
| | -352.74 | -330.16 | 74.06 | -231.64 | 174.34 | | |
| | -50.35 | 361.15 | 338.07 | -36.18 | 105.79 | | |
| 64 | -472.79 | 204.93 | -198.97 | 375.33 | 503.32 | 0.015 | -36.36 |
| | -144.45 | 380.01 | -352.23 | -145.81 | 188.57 | | |
| | 220.32 | 376.90 | 199.84 | 409.37 | 248.41 | | |
| | 108.53 | 471.50 | -200.90 | 122.89 | 362.67 | | |
| 65 | -91.60 | -803.49 | -629.77 | -731.26 | -246.86 | 0.007 | 30.00 |
| | 854.41 | 646.35 | -125.94 | -173.97 | 76.81 | | |
| | 262.38 | 107.78 | 186.11 | 676.65 | 605.54 | | |
| | 662.87 | 274.65 | 31.09 | 51.18 | 135.09 | | |
| **average rmsd** | | | | | | **0.0123** | **7.52** |

Table 3.8 Comparison of average rmsd's in terms of percentage gain

| Model | Systems | average rmsd | | $gain_{lit}^{woce}$ % | $gain_{woce}^{wce}$ % | $gain_{lit}^{wce}$ % |
|---|---|---|---|---|---|---|
| NRTL | Ternary | literature | 0.0068 | | | |
| | | woce | 0.0043 | 36.77 | 11.63 | 44.12 |
| | | wce | 0.0038 | | | |
| | Quaternary | literature | 0.0069 | | | |
| | | woce | 0.0051 | 26.09 | 9.80 | 33.33 |
| | | wce | 0.0046 | | | |
| | Quinary | literature | 0.0077 | | | |
| | | woce | 0.0057 | 25.97 | 7.02 | 31.17 |
| | | wce | 0.0053 | | | |
| **average rmsd gain** | | | | **34.46** | **11.38** | **41.67** |
| UNIQUAC | Ternary | literature | 0.0074 | | | |
| | | woce | 0.0059 | 20.27 | 11.86 | 29.73 |
| | | wce | 0.0052 | | | |
| | Quaternary | literature | n.a. | | | |
| | | woce | 0.0079 | n.a. | 17.72 | n.a. |
| | | wce | 0.0065 | | | |
| | Quinary | literature | n.a. | | | |
| | | woce | 0.0133 | n.a. | 7.52 | n.a. |
| | | wce | 0.0123 | | | |
| **average rmsd gain** | | | | **20.27** | **12.21** | **29.73** |

n.a.: not available/not applicable

While implementing the closure equation for ternary systems all the six possibilities of parameter elimination have been tried. It was observed that the rmsd values change significantly with the eliminated parameters. This is due to the different search path adopted by the optimization procedure for different eliminated parameter to reach the final optimum point. The interaction parameters with closure equation given in Table 3.2 and Table 3.5 correspond to the lowest rmsd for the six possibilities.

The choice of the parameters to be eliminated to implement the closure equations plays a very important role in decreasing the rmsd values for quaternary and quinary systems. All likely feasible combinations of parameter elimination have been tried; 8 for quaternary and 21 for quinary systems. The rmsd values were vary significantly with the eliminated parameters. Reasons explained for the ternary systems apply here also for this variation. Additionally, the larger deviation is due to the higher dimension of optimization problem encountered. The interaction parameters with closure equations

given in Table 3.3, Table 3.4, Table 3.6 and Table 3.7 correspond to the lowest rmsd of all likely feasible combination of parameter elimination.

It is observed that for some systems, without implementation of closure equation/s exhibit better rmsd values than with closure equation/s. It is also observed that for some systems rmsd values reported in the literature are better. The expected reason could be the biased experimental error in the reported liquid-liquid equilibrium data.

## 3.4 Conclusions

Genetic algorithm has been applied with closure equation/s to estimate binary interaction parameters for liquid-liquid aromatic extraction systems. Root mean square deviation values with closure equation/s are found to be better than without closure equation/s. The average root mean square deviation value with closure equation/s is approximately 12 percent better than those without closure equation/s. Overall percentage gain is approximately 42 percent better for NRTL model and 30 percent better for UNIQUAC model, than literature.

## References


[1] E. Hala, "Note to Bruin-Prausnitz One-Parameter and Palmer-Smith Two-Parameter Local Composition Equation", *Industrial & Engineering Chemistry Process Design and Development* **11** (1972) 638.

[2] G. Varheygi, C. H. Eon, "Correlation of the Free Energy Equation Parameters from Ternary Liquid-Liquid Equilibria data", *Industrial and Engineering Chemistry Fundamentals* **16** (1977) 182.

[3] S. A. Ahmad, "LLE experimentation parameter estimation and validation for aromatic extraction systems", *PhD Thesis*, Indian Institute of Technology Kanpur, 2003.

[4] S. A. Ahmad, A. Khanna, "Closure Equations in the Estimation of Binary Interaction Parameters", *Korean Journal of Chemical Engineering* **20** (2003) 736.

# Chapter 4

# SIMULATION OF AROMATIC RECOVERY FLOWSHEET USING LIQUID-LIQUID EXTRACTION

## 4.1 Introduction

Aromatic Recovery Unit (ARU) of a refinery is the section which separates aromatics and non-aromatics components from naphtha with the help of a suitable solvent. Procurement of data was from Corporate BPCL R&D Centre, Noida. The simulation is basically for a 650 MT/D of naphtha feed. The flowsheet is divided into three basic sections.

Extraction section, Solvent Recovery section, and Fractionation section

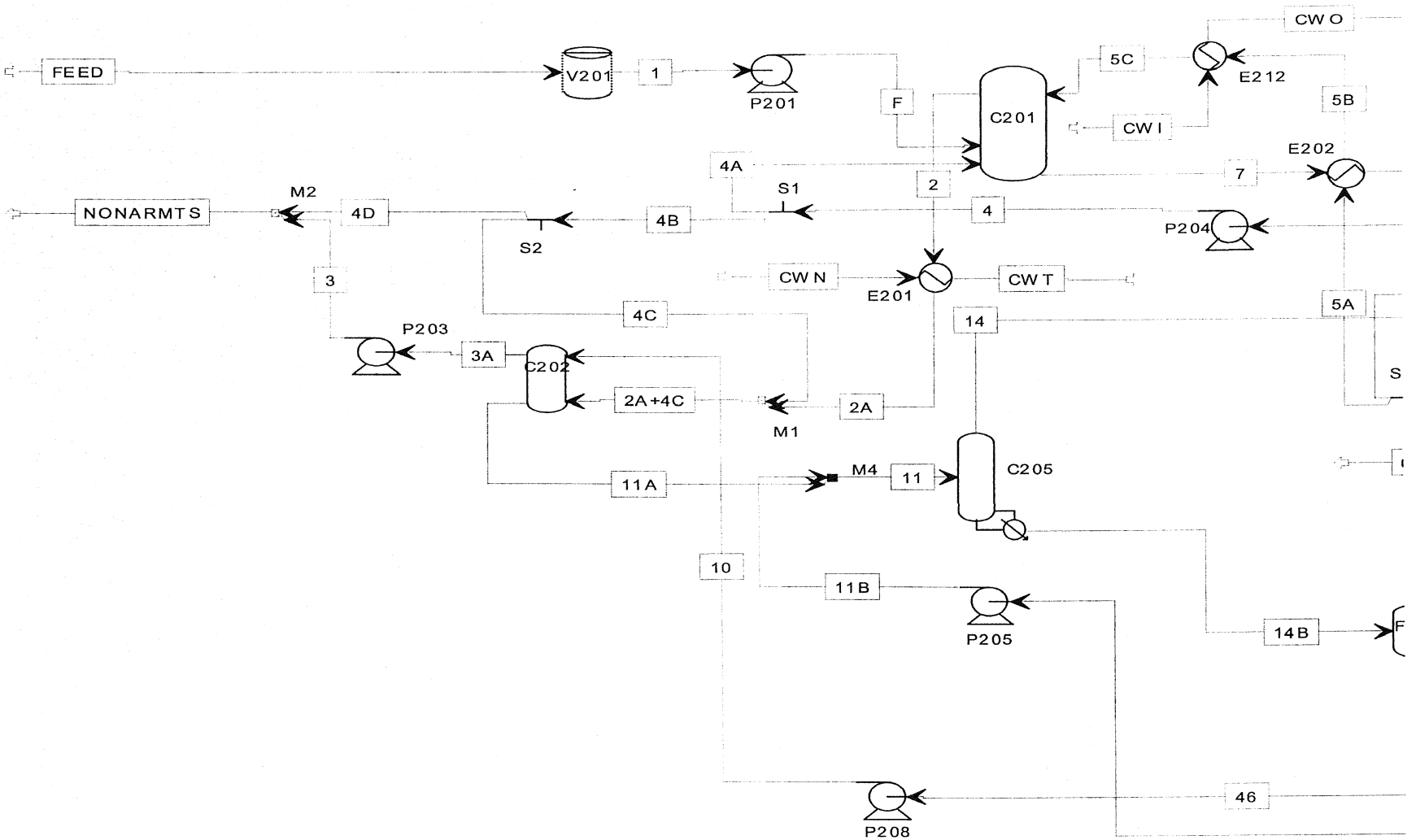
Extraction section and solvent recovery section s have several recycle loops but the fractionation section is separate from the other two sections and has only one input stream coming from integrated extraction and solvent recovery section. Aspen plus 10.2, a sequential modular simulation software package is used to simulate the process.

## 4.2 Process Description

Simulation flowsheet of aromatic recovery unit is shown in Flowsheet 4.1.

### 4.2.1 Extraction section

Naphtha is fed to the extraction column, C201, along with the extract recycle stream, 4A, and recycled lean solvent stream, 5C. The raffinate stream, 2, leaving from the top of C201 is cooled in exchanger E201 and mixed with stream 4C in mixer M1. The stream 2A+4C from mixer M1 is fed to the raffinate wash column, C202, to extract sulfolane from the raffinate stream, 2, with the help of water stream, 10, coming from the decanter, V203, as a solvent. It is important to state here that sulfolane is not a solvent with reference to column C202. Non-aromatics stream, 3A, from the top of C202 is pumped and mixed with stream 4D in M2; this mixed stream, NONARMTS, forms the non-aromatic products from the ARU section. The extract stream, 7, from the bottom of C201 is heated by the lean solvent stream, 5A, in heat exchanger E202. Stream 5B is the recycle solvent to C201. The heated steam 7A after mixing with secondary solvent stream, 6, in mixer M3 is fed to the extract stripper, C203, as stream 7A+6.




Flowsheet 4.1 Simulation flowsheet of extraction aromatic recovery unit

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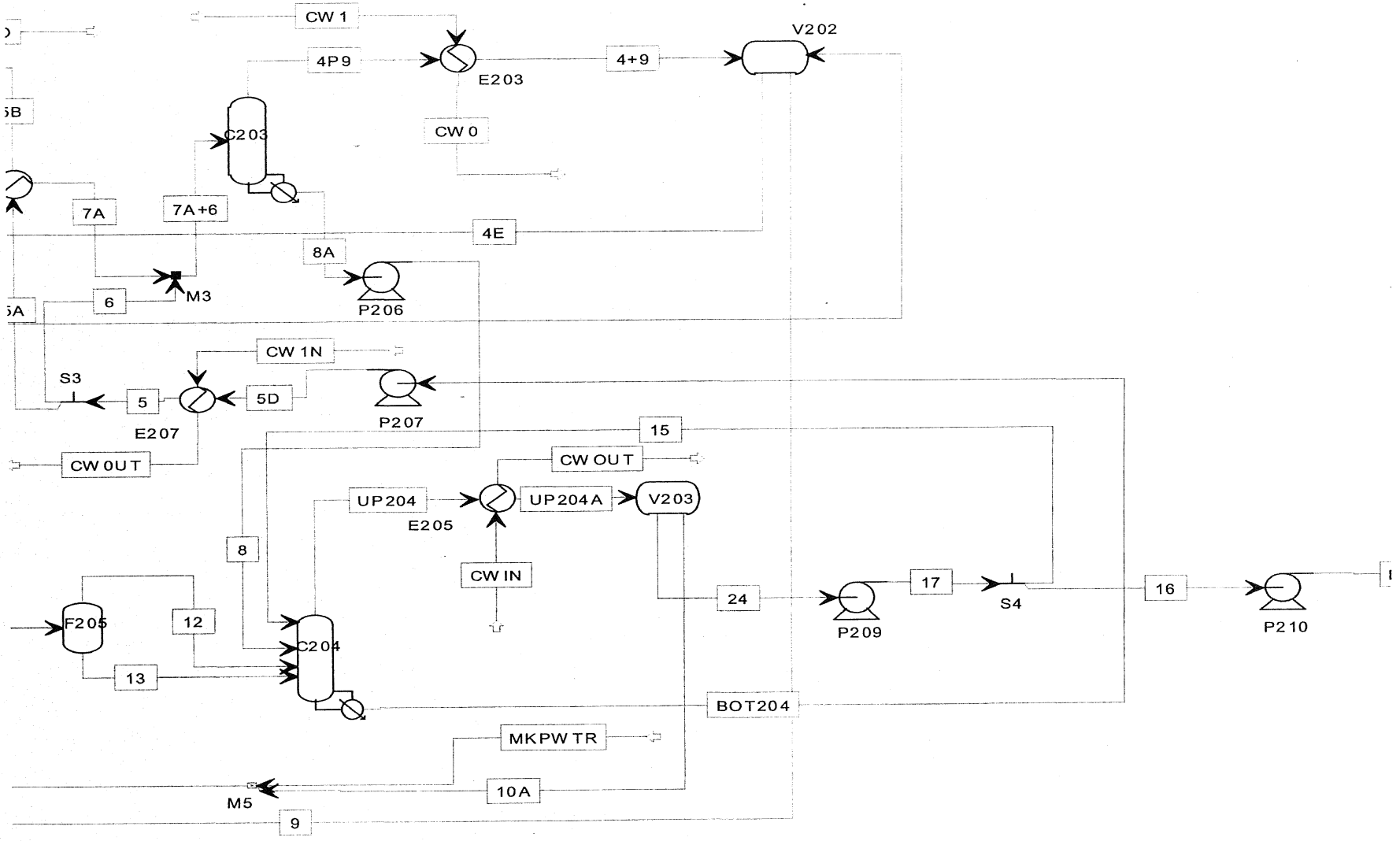


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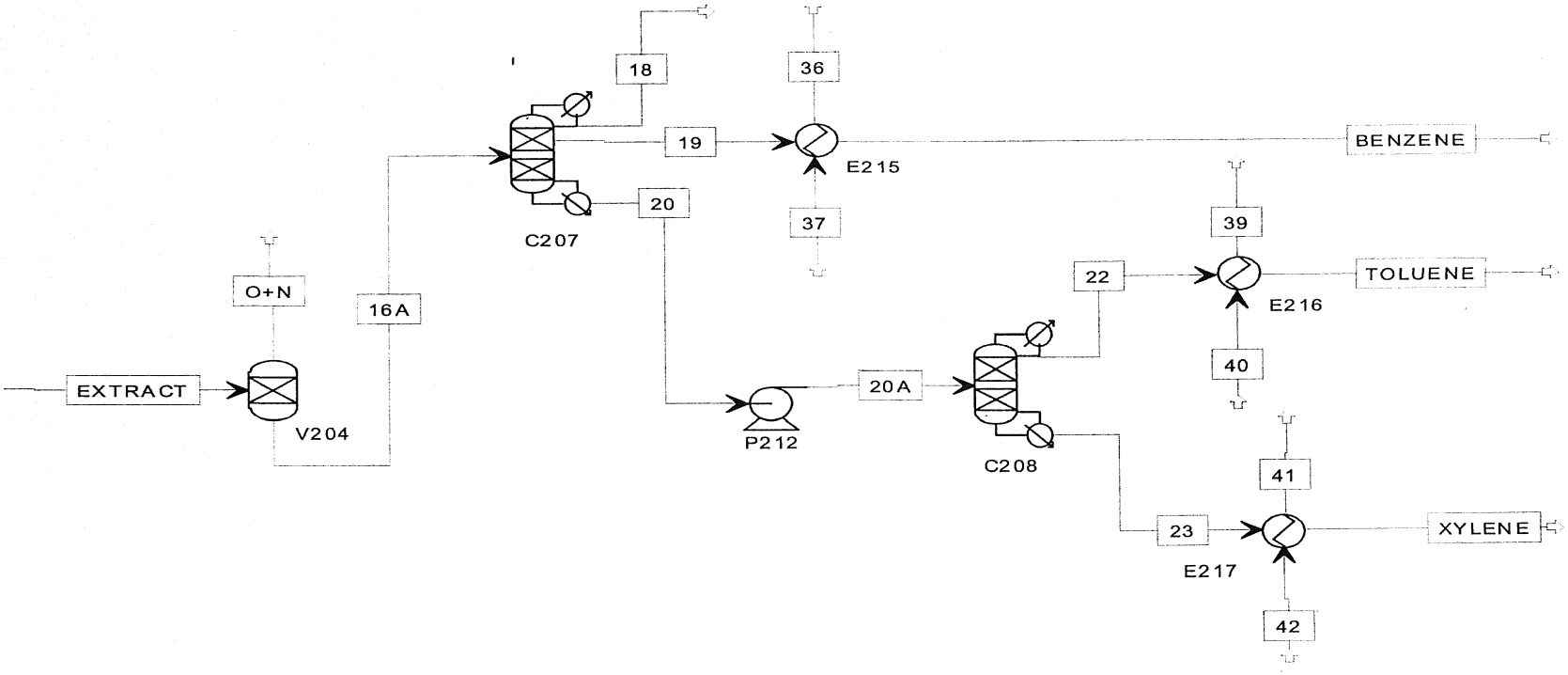
18
36
19
E215
BENZENE
C207
20
37
39
22
TOLUENE
E216
O+N
16A
40
EXTRACT
V204
20A
P212
C208
41
23
XYLENE
E217
42

Stream 8A from bottom of C203 is pumped and fed to the solvent recovery column, C204, as stream 8. The overhead of C203 is cooled in exchanger E203 and fed to the decanter V202 to remove water. Stream 4E from V202 contains non-aromatics along with some quantity of aromatics. Part of this is pumped and recycled back to C201 as 4A.

### 4.2.2 Solvent Recovery Section

Water stream, 9 from V202 is pumped and mixed with extract stream, 11A from the bottom of the C202 in mixer M4. This mixed stream, 11 is fed to the water stripper, C205. Water and sulfolane mixture, 14B, from the bottom of C205 is flashed and fed to the solvent recovery column, C204. Water and aromatics mixture, 14, from top of C205 is fed to V202. Water is separated from the stream UP204A in decanter V203 and pumped back to raffinate wash column, C202. Part of the aromatics stream, 17 recovered from V203 is recycled back to C204 as external reflux, 15.

### 4.2.3 Fractionation Section

Major part of the stream 17 comes to the fractionation section as, EXRACT. This stream is clay treated in clay tower V204 to remove traces of olefins, naphthenes and other impurities. The clay treated extract, 16A, is directed to the aromatics fractionation section where high-purity benzene, toluene, and sometimes mixed xylenes are recovered. Aromatics fractionation section is a series of two distillation column; Benzene column, C207, and toluene column, C208. Benzene product, 19, is withdrawn from the $5^{th}$ tray from top of C207. Bottom of C207, 20, is pumped and fed to C208. Toluene is recovered as overhead of the toluene column, C208.

## 4.3 Feed composition

The composition of the feed stream, FEED, entering the extractor, C201 is shown in Table 4.1. Feed consists of components from all Paraffin, Iso-paraffin, Olefin, Naphthene and Aromatic (PIONA) families.

## 4.4 Individual Column Simulation

It is always recommended to simulate the important unit blocks of a flowsheet individually before attempting complete flowsheet simulation. This approach is used to

start the simulation of ARU. Initially two extraction columns, C201 and C202 and five distillation columns, C203, C204, C205, C207 and C208 were simulated separately.

Table 4.1 Feed compositions (Naphtha)

| Components | MT/D | Family |
|---|---|---|
| n-Pentane | 29.720 | n-Paraffin |
| n-Hexane | 54.940 | n-Paraffin |
| Iso-Pentane | 25.840 | Iso-paraffin |
| 2-Methyl pentane | 130.180 | Iso-paraffin |
| Cis-2-Hexene | 6.790 | Olefin |
| Methylcyclopentane | 13.450 | Naphthene |
| Benzene | 299.970 | Aromatic |
| Toluene | 85.820 | Aromatic |
| *o*-Xylene | 3.290 | Aromatic |
| Sulfolane | 0.000 | Solvent |
| Total | 650.000 | |

### 4.4.1 Input specifications

Design specifications for various columns are given in Table 4.2.

Table 4.2 Design specifications of columns for extraction aromatic recovery unit

| Block | Diameter, m | Number of actual stages | Feed stages | Product stages | Temperature, C | | Pressure, Kg/sqcmg | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Top | Bottom | Top | Bottom | Drop |
| C201 | 2.2 | 57 | 1,56,57 | 1,57 | 83.200 | 61.200 | 4.990 | 8.050 | |
| C202 | 1.8 | 40 | 1,40 | 1,40 | 40.000 | 42.000 | 2.047 | | 3.400 |
| C203 | 2.0 | 40 | 1 | 1,40 | | | 1.488[a] | 1.700[a] | |
| C204 | 2.4 | 35 | 1,16,34,34 | 1,35 | | | 0.564[a] | | 0.053 |
| C205 | 0.61 | 5 | 1 | 1,5 | | | 0.750 | 0.780 | |
| C207 | 2.2 | 43 | 27 | 1,5,43 | | | 0.470 | | 487.000[b] |
| C208 | 0.8 | 50 | 22 | 1,50 | | | 0.200 | | 555.000[b] |

[a] Kg/sqcm: [b] mm-water

Design data are used for tuning the operating variables such as reflux rate, distillate rate, boilup ratio and reflux ratio. The prime aim of simulation at this stage is to get approximate values of these tuned variables to be used in complete flowsheet simulation. RADFRAC subroutine is used for stripper and distillation columns and EXTRACT subroutine is used for extraction columns. Initial operating variables used for different columns are given in Table 4.3.

Table 4.3 Initial operating specifications of columns for extraction aromatic recovery unit

| Specification | C201 | C202 | C203 | C204 | C205 | C207 | C208 |
|---|---|---|---|---|---|---|---|
| Reflux rate, MT/D | | | | | | 609.0000 | 75.4000 |
| Distillate rate, MT/D | | | 157.0000 | | | | |
| Boilup ratio, mole | | | | 0.1661 | 0.6380 | 7.9140 | 50.800 |
| Benzene product rate, MT/D | | | | | | 279.0000 | |

### 4.4.2 Property method

Choice of an appropriate physical and thermodynamic property method plays an important part in simulation of process flowsheet. In the present work, different property methods have been chosen. The flowsheet has two liquid-liquid extraction columns and five distillation columns. As the liquid-liquid equilibria are important in case of liquid-liquid extraction, UNIF-LL property method has been used for C201 and C202. RK-SOAVE property method is used in all distillation columns, as vapor-liquid equilibria are important in case of distillation. UNIF-LL is used as global property method.

### 4.4.3. Efficiencies

ChemSep is used for estimating the murphree efficiencies for different individual column. We considered non-equilibrium model. There are few limitations in using ChemSep software for determining the efficiency. One of the most serious drawbacks is that we can take only ten components at a time in ChemSep simulation. To overcome this problem, we choose components above the light key and below the heavy key having dominant mass fractions. This can provide a good approximation for the efficiencies of the columns. ChemSep input specifications are given in Table 4.4. The supplied design data are used instead of default values in ChemSep. The data, which are not available, are taken from literature [1]. Murphree efficiency for column C203, C204, C205, C207 and C208 calculated from ChemSep are reported respectively in Table 4.5-4.9. Efficiency plot as obtained from ChemSep are shown in Appendix B. For C201 and C202 ChemSep gives efficiency of 1 for all components on all stages. This is not feasible; hence average column efficiency of 0.3 is used for both C201 and C202 [2]. These efficiencies are used as input in ASPEN PLUS simulation.

Table 4.4 Input Specifications of ChemSep individual block simulation for extraction aromatic recovery unit

| Specifications | C201 | C202 | C203 | C204 | C205 | C207 | C208 |
|---|---|---|---|---|---|---|---|
| Operation | Non Equilibrium | Non Equilibrium | Non Equilibrium | Non Equilibrium | Non Equilibrium | Non Equilibrium | Non Equilibrium |
| Type | Simple Extractor | Simple Extractor | Extractive Distillation | Simple Distillation | Reboiled Stripper | Simple Distillation | Simple Distillation |
| Column internals | Sieve tray | Sieve tray | Sieve tray | Sieve tray | Sieve tray | Structured packing | Structured packing |
| Section height, m | n.a. | n.a. | n.a. | n.a. | n.a. | 19.458, 13.536 | 14.934, 21.222 |
| Column diameter, m | 2.200 | 1.800 | 2.000 | 2.400 | 0.610 | 2.200 | 0.800 |
| Packing type | | | | | | Sulzer BX | Sulzer BX |
| Tray spacing, m | 0.717 | 0.475 | 0.805 | 0.800 | 0.940 | | |
| Number of flow passes | 1 | 1 | 1 | 1 | 1 | | |
| Liquid flow path length, m | 1.600 | 1.600 | 1.600 | 1.600 | 1.600 | | |
| Downcomer clearance, m | 0.0381 | 0.0381 | 0.0381 | 0.0381 | 0.0381 | | |
| Deck thickness, m | 0.00254 | 0.00254 | 0.00254 | 0.00254 | 0.00254 | | |
| Hole diameter, m | 0.005-0.012 | 0.005-0.012 | 0.005-0.012 | 0.005-0.012 | 0.005-0.012 | | |
| Hole pitch, m | 0.032 | 0.032 | 0.032 | 0.032 | 0.032 | | |
| Active area, % total | 55.000 | 48.000 | 82.000 | 60.000 | 80.000 | | |
| Total hole area, % active | 10.000 | 10.000 | 10.000 | 10.000 | 10.000 | | |
| Downcomer area, % total | 12.000 | 12.000 | 12.000 | 12.000 | 12.000 | | |
| Weir type | Segmental | Segmental | Segmental | Segmental | Segmental | | |
| Weir length, m | 1.540 | 1.260 | 1.400 | 1.680 | 0.427 | | |
| Weir height, m | 0.040 | 0.040 | 0.040 | 0.040 | 0.040 | | |

Table 4.5 Murphree Efficiencies for C203

| Stage | N-P | N-H | 2-MB | 2-MP | C-2-HE | MCP | BE | TOL | OX | TMS |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.8878 | 0.8860 | 0.8855 | 0.8791 | 0.8343 | 0.8873 | 0.8988 | 0.8991 | 0.9058 | 0.9280 |
| 2 | 0.5366 | 0.5506 | 0.4964 | 0.4266 | 0.9983 | 0.5381 | 0.5744 | 0.5771 | 0.5986 | 0.6505 |
| 3 | 0.5301 | 0.5486 | 0.4919 | 0.3660 | 0.7179 | 0.5377 | 0.5708 | 0.5703 | 0.5865 | 0.6387 |
| 4 | 0.5247 | 0.5468 | 0.4878 | 0.1683 | 0.6477 | 0.5383 | 0.5692 | 0.5672 | 0.5811 | 0.6331 |
| 5 | 0.5199 | 0.5450 | 0.4841 | 1.0000 | 0.6149 | 0.5397 | 0.5687 | 0.5657 | 0.5780 | 0.6296 |
| 6 | 0.5158 | 0.5432 | 0.4808 | 0.8014 | 0.5955 | 0.5418 | 0.5687 | 0.5650 | 0.5758 | 0.6267 |
| 7 | 0.5121 | 0.5414 | 0.4777 | 0.6723 | 0.5826 | 0.5447 | 0.5692 | 0.5646 | 0.5740 | 0.6239 |
| 8 | 0.5088 | 0.5394 | 0.4750 | 0.6248 | 0.5733 | 0.5484 | 0.5701 | 0.5646 | 0.5725 | 0.6210 |
| 9 | 0.5060 | 0.5373 | 0.4725 | 0.5999 | 0.5662 | 0.5528 | 0.5715 | 0.5650 | 0.5711 | 0.6179 |
| 10 | 0.5034 | 0.5347 | 0.4703 | 0.5845 | 0.5607 | 0.5578 | 0.5733 | 0.5658 | 0.5701 | 0.6148 |
| 11 | 0.5011 | 0.5317 | 0.4682 | 0.5741 | 0.5562 | 0.5632 | 0.5756 | 0.5669 | 0.5694 | 0.6115 |
| 12 | 0.4990 | 0.5277 | 0.4663 | 0.5666 | 0.5526 | 0.5688 | 0.5782 | 0.5684 | 0.5690 | 0.6082 |
| 13 | 0.4972 | 0.5225 | 0.4645 | 0.5609 | 0.5496 | 0.5744 | 0.5812 | 0.5703 | 0.5690 | 0.6050 |
| 14 | 0.4955 | 0.5152 | 0.4629 | 0.5566 | 0.5471 | 0.5795 | 0.5844 | 0.5725 | 0.5693 | 0.6019 |
| 15 | 0.4939 | 0.5045 | 0.4613 | 0.5532 | 0.5450 | 0.5839 | 0.5875 | 0.5747 | 0.5698 | 0.5988 |
| 16 | 0.4924 | 0.4873 | 0.4599 | 0.5505 | 0.5432 | 0.5873 | 0.5903 | 0.5767 | 0.5703 | 0.5959 |
| 17 | 0.4910 | 0.4560 | 0.4584 | 0.5483 | 0.5416 | 0.5895 | 0.5926 | 0.5782 | 0.5705 | 0.5930 |
| 18 | 0.4897 | 0.3826 | 0.4570 | 0.5465 | 0.5402 | 0.5906 | 0.5940 | 0.5791 | 0.5703 | 0.5900 |
| 19 | 0.4883 | 0.0207 | 0.4554 | 0.5448 | 0.5388 | 0.5904 | 0.5945 | 0.5792 | 0.5694 | 0.5867 |
| 20 | 0.4868 | 1.0000 | 0.4538 | 0.5431 | 0.5374 | 0.5889 | 0.5939 | 0.5783 | 0.5678 | 0.5831 |
| 21 | 0.4851 | 0.7487 | 0.4520 | 0.5412 | 0.5358 | 0.5862 | 0.5923 | 0.5763 | 0.5652 | 0.5790 |
| 22 | 0.4821 | 0.6719 | 0.4499 | 0.5390 | 0.5338 | 0.5821 | 0.5896 | 0.5733 | 0.5618 | 0.5742 |
| 23 | 0.4808 | 0.6370 | 0.4474 | 0.5362 | 0.5313 | 0.5766 | 0.5858 | 0.5694 | 0.5574 | 0.5687 |
| 24 | 0.4779 | 0.6155 | 0.4446 | 0.5328 | 0.5283 | 0.5697 | 0.5811 | 0.5644 | 0.5521 | 0.5626 |
| 25 | 0.4745 | 0.5997 | 0.4412 | 0.5287 | 0.5245 | 0.5611 | 0.5756 | 0.5588 | 0.5461 | 0.5558 |
| 26 | 0.4707 | 0.5867 | 0.4375 | 0.5239 | 0.5202 | 0.5504 | 0.5695 | 0.5525 | 0.5396 | 0.5485 |
| 27 | 0.4663 | 0.5754 | 0.4333 | 0.5187 | 0.5154 | 0.5368 | 0.5631 | 0.5460 | 0.5328 | 0.5410 |
| 28 | 0.4617 | 0.5651 | 0.4289 | 0.5131 | 0.5101 | 0.5184 | 0.5567 | 0.5396 | 0.5259 | 0.5333 |
| 29 | 0.4569 | 0.5558 | 0.4244 | 0.5073 | 0.5048 | 0.4901 | 0.5505 | 0.5338 | 0.5196 | 0.5260 |
| 30 | 0.4522 | 0.5474 | 0.4199 | 0.5017 | 0.4995 | 0.4348 | 0.5449 | 0.5296 | 0.5143 | 0.5193 |
| 31 | 0.4477 | 0.5399 | 0.4156 | 0.4963 | 0.4944 | 0.2480 | 0.5401 | 0.5285 | 0.5114 | 0.5140 |
| 32 | 0.4435 | 0.5333 | 0.4117 | 0.4914 | 0.4897 | 1.0000 | 0.5361 | 0.5334 | 0.5139 | 0.5113 |
| 33 | 0.4397 | 0.5276 | 0.4081 | 0.4870 | 0.4855 | 0.7910 | 0.5326 | 0.5486 | 0.5289 | 0.5154 |
| 34 | 0.4364 | 0.5227 | 0.4050 | 0.4831 | 0.4818 | 0.6935 | 0.5283 | 0.5777 | 0.5668 | 0.5375 |
| 35 | 0.4335 | 0.5186 | 0.4022 | 0.4798 | 0.4786 | 0.6574 | 0.5191 | 0.6165 | 0.6252 | 0.5948 |
| 36 | 0.4309 | 0.5151 | 0.3998 | 0.4768 | 0.4757 | 0.6390 | 0.4908 | 0.6517 | 0.6761 | 0.6724 |
| 37 | 0.4285 | 0.5119 | 0.3976 | 0.4741 | 0.4731 | 0.6282 | 0.3516 | 0.6744 | 0.7032 | 0.7215 |
| 38 | 0.4258 | 0.5085 | 0.3950 | 0.4710 | 0.4702 | 0.6210 | 1.0000 | 0.6853 | 0.7140 | 0.7406 |
| 39 | 0.4216 | 0.5040 | 0.3910 | 0.4666 | 0.4661 | 0.6161 | 0.7924 | 0.6890 | 0.7190 | 0.7495 |
| 40 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |

N-P: n-pentane; N-H: n-hexane; 2-MB: 2-methyl butane; 2-MP: 2-methyl pentane; C-2-HE: cis-2-hexene; MCP: Methylcyclopentane; BZ: benzene; TOL: Toluene; OX: *o*-xylene; TMS: sulfolane

Table 4.6 Murphree Efficiencies for C204

| Stage | BE | TOL | TMS | Stage | BE | TOL | TMS |
|---|---|---|---|---|---|---|---|
| 1 | 0.3820 | 0.5817 | 0.4077 | 19 | 0.3099 | 0.3542 | 0.3225 |
| 2 | 0.3556 | 0.3812 | 0.3608 | 20 | 0.2991 | 0.3425 | 0.3127 |
| 3 | 0.3764 | 0.3695 | 0.3748 | 21 | 0.2969 | 0.3401 | 0.3119 |
| 4 | 0.3859 | 0.3700 | 0.3823 | 22 | 0.2965 | 0.3397 | 0.3129 |
| 5 | 0.3907 | 0.3722 | 0.3865 | 23 | 0.2964 | 0.3396 | 0.3143 |
| 6 | 0.4065 | 0.3859 | 0.4019 | 24 | 0.2964 | 0.3396 | 0.3158 |
| 7 | 0.4701 | 0.4463 | 0.4651 | 25 | 0.2964 | 0.3396 | 0.3173 |
| 8 | 0.5001 | 0.4843 | 0.4969 | 26 | 0.2964 | 0.3396 | 0.3188 |
| 9 | 0.5056 | 0.4918 | 0.5028 | 27 | 0.2964 | 0.3396 | 0.3204 |
| 10 | 0.5063 | 0.4928 | 0.5036 | 28 | 0.2964 | 0.3396 | 0.3219 |
| 11 | 0.5064 | 0.4929 | 0.5037 | 29 | 0.2964 | 0.3396 | 0.3233 |
| 12 | 0.5065 | 0.4930 | 0.5038 | 30 | 0.2964 | 0.3396 | 0.3248 |
| 13 | 0.5066 | 0.4931 | 0.5039 | 31 | 0.2964 | 0.3396 | 0.3261 |
| 14 | 0.5069 | 0.4934 | 0.5042 | 32 | 0.2964 | 0.3396 | 0.3274 |
| 15 | 0.5072 | 0.4938 | 0.5045 | 33 | 0.2964 | 0.3396 | 0.3286 |
| 16 | 0.9738 | 0.9602 | 0.9718 | 34 | 0.2964 | 0.3396 | 0.3295 |
| 17 | 0.4250 | 0.4928 | 0.4394 | 35 | 1.0000 | 1.0000 | 1.0000 |
| 18 | 0.3539 | 0.4015 | 0.3659 | | | | |

Table 4.7 Murphree Efficiencies for C205

| Stage | N-P | N-H | 2-MB | 2-MP | C-2-HE | MCP | BE | TOL | WATER | TMS |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.9153 | 0.9133 | 0.9152 | 0.9132 | 0.9160 | 0.9129 | 0.8964 | 0.8969 | 0.9096 | 0.8016 |
| 2 | 0.0146 | 0.0112 | 0.0119 | 0.0082 | 0.0317 | 0.1006 | 0.3551 | 0.3208 | 0.1813 | 0.4732 |
| 3 | 0.0146 | 0.0111 | 0.0119 | 0.0082 | 0.0317 | 0.1005 | 0.3550 | 0.3207 | 0.3154 | 0.4709 |
| 4 | 0.0146 | 0.0111 | 0.0119 | 0.0082 | 0.0316 | 0.1005 | 0.3550 | 0.3207 | 0.4175 | 0.4704 |
| 5 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |

Table 4.8 Murphree efficiencies for C207

| Stage | BE | TOL | OX | Stage | BE | TOL | OX |
|---|---|---|---|---|---|---|---|
| 1 | 1.0000 | 1.0000 | 1.0000 | 23 | 0.8130 | 0.8101 | 0.8219 |
| 2 | 0.8200 | 0.8200 | 0.8194 | 24 | 0.8128 | 0.7913 | 0.8219 |
| 3 | 0.8201 | 0.8201 | 0.8193 | 25 | 0.9989 | 1.0000 | 0.6086 |
| 4 | 0.8201 | 0.8201 | 0.8194 | 26 | 0.8308 | 0.8308 | 0.8262 |
| 5 | 0.8202 | 0.8202 | 0.8196 | 27 | 0.8286 | 0.8286 | 0.8243 |
| 6 | 0.8202 | 0.8202 | 0.8199 | 28 | 0.8268 | 0.8268 | 0.8227 |
| 7 | 0.8202 | 0.8202 | 0.8202 | 29 | 0.8256 | 0.8256 | 0.8217 |
| 8 | 0.8201 | 0.8201 | 0.8206 | 30 | 0.8247 | 0.8247 | 0.8212 |
| 9 | 0.8198 | 0.8198 | 0.8210 | 31 | 0.8242 | 0.8242 | 0.8214 |
| 10 | 0.8192 | 0.8192 | 0.8213 | 32 | 0.8239 | 0.8239 | 0.8233 |
| 11 | 0.8184 | 0.8184 | 0.8215 | 33 | 0.8238 | 0.8237 | 0.8277 |

*(continued on next page)*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 12 | 0.8174 | 0.8174 | 0.8216 | 34 | 0.8237 | 0.8236 | 0.8323 |
| 13 | 0.8164 | 0.8164 | 0.8216 | 35 | 0.8236 | 0.8234 | 0.8346 |
| 14 | 0.8155 | 0.8155 | 0.8217 | 36 | 0.8236 | 0.8226 | 0.8354 |
| 15 | 0.8148 | 0.8148 | 0.8217 | 37 | 0.8236 | 0.8189 | 0.8356 |
| 16 | 0.8142 | 0.8142 | 0.8217 | 38 | 0.8235 | 1.0000 | 0.8357 |
| 17 | 0.8138 | 0.8138 | 0.8218 | 39 | 0.8235 | 0.8397 | 0.8357 |
| 18 | 0.8137 | 0.8137 | 0.8219 | 40 | 0.8235 | 0.8366 | 0.8357 |
| 19 | 0.8135 | 0.8135 | 0.8219 | 41 | 0.8235 | 0.8360 | 0.8358 |
| 20 | 0.8133 | 0.8133 | 0.8219 | 42 | 0.8236 | 0.8360 | 0.8359 |
| 21 | 0.8132 | 0.8130 | 0.8219 | 43 | 1.0000 | 1.0000 | 1.0000 |
| 22 | 0.8131 | 0.8124 | 0.8219 | | | | |

Table 4.9 Murphree efficiencies for C208

| Stage | TOL | OX | Stage | TOL | OX | Stage | TOL | OX |
|---|---|---|---|---|---|---|---|---|
| 1 | 1.0000 | 1.0000 | 18 | 1.0000 | 0.9211 | 35 | 0.8189 | 0.8189 |
| 2 | 0.7834 | 0.7834 | 19 | 0.8594 | 0.8187 | 36 | 0.8189 | 0.8189 |
| 3 | 0.7833 | 0.7833 | 20 | 0.8196 | 0.8170 | 37 | 0.8189 | 0.8189 |
| 4 | 0.7833 | 0.7833 | 21 | 1.0000 | 1.0000 | 38 | 0.8189 | 0.8189 |
| 5 | 0.7833 | 0.7833 | 22 | 0.8189 | 0.8189 | 39 | 0.8189 | 0.8189 |
| 6 | 0.7833 | 0.7833 | 23 | 0.8189 | 0.8189 | 40 | 0.8189 | 0.8189 |
| 7 | 0.7833 | 0.7833 | 24 | 0.8189 | 0.8189 | 41 | 0.8190 | 0.8190 |
| 8 | 0.7833 | 0.7833 | 25 | 0.8189 | 0.8189 | 42 | 0.8190 | 0.8190 |
| 9 | 0.7833 | 0.7833 | 26 | 0.8189 | 0.8189 | 43 | 0.8191 | 0.8191 |
| 10 | 0.7832 | 0.7836 | 27 | 0.8189 | 0.8189 | 44 | 0.8194 | 0.8194 |
| 11 | 0.7826 | 0.7866 | 28 | 0.8189 | 0.8189 | 45 | 0.8198 | 0.8198 |
| 12 | 0.7660 | 0.8200 | 29 | 0.8189 | 0.8189 | 46 | 0.8204 | 0.8204 |
| 13 | 0.6000 | 1.0000 | 30 | 0.8189 | 0.8189 | 47 | 0.8210 | 0.8210 |
| 14 | 0.0001 | 0.0001 | 31 | 0.8189 | 0.8189 | 48 | 0.8208 | 0.8208 |
| 15 | 0.0001 | 0.0336 | 32 | 0.8189 | 0.8189 | 49 | 0.8188 | 0.8188 |
| 16 | 0.0001 | 0.3696 | 33 | 0.8189 | 0.8189 | 50 | 1.0000 | 1.0000 |
| 17 | 1.0000 | 1.0000 | 34 | 0.8189 | 0.8189 | | | |

## 4.5 Simulation of complete Aromatic Recovery Unit

After simulating each column separately, we proceed for flowsheet connectivity. Flowsheet connectivity can be done in two ways:

- Make backup file of one flowsheet using export option. Open other flowsheet and import this backup file and merge it with existing file. In that case care should be taken and one should be careful of merging common streams. The nomenclature and sequence of components must be same. Both flowsheets must have units and

properties common. Run the flow sheet every time after merging. In the same way, several flowsheets can be merged into an integrated flowsheet.

- Simulate one column, then add other column in the same flowsheet and run each time.

The main drawback in the first method is that it makes flowsheet more complex, which is hard to understand. Nomenclature of design spec and sensitivity analysis should not be the same i.e. if DS1 is defined in the first flowsheet, this should not be defined in other flowsheet. Here the other method is used for connectivity of flowsheets in which the error probability is far less than the first method. In this method, we add the block one by one and see the effect of each block. We solve different recycles in different flowsheets and after successful simulation; we include them in our integrated flowsheet. Specifications of other blocks are given in Table 4.10-4.12.

Table 4.10 Specifications of pumps for extraction aromatic recovery unit

| Block | Specification | Stream | Value |
|---|---|---|---|
| P201 | Discharge pressure | F | 7.000 bar |
| P203 | Discharge pressure | 3 | 5.000 kg/sqcm |
| P204 | Discharge pressure | 4 | 5.000 kg/sqcm |
| P205 | Discharge pressure | 11B | 6.500 kg/sqcm |
| P206 | Discharge pressure | 8 | 5.000 kg/sqcmg |
| P207 | Discharge pressure | 5D | 5.000 kg/sqcm |
| P208 | Discharge pressure | 10 | 2.500 kg/sqcm |
| P209 | Discharge pressure | 17 | 1.610 kg/sqcm |
| P210 | Discharge pressure | EXTRACT | 13.529 kg/sqcmg |
| P212 | Discharge pressure | 20A | 6.000 kg/sqcmg |

Table 4.11 Specifications of heat exchangers for extraction aromatic recovery unit

| Block | Specification | Stream | Value |
|---|---|---|---|
| E201 | Hot stream outlet temperature | 2A | 40.8000 C |
| E202 | Cold stream outlet temperature | 7A | 79.3000 C |
| E203 | Hot stream outlet vapor fraction | 4+9 | 0.000 |
| E205 | Hot stream outlet vapor fraction | UP204A | 0.000 |
| E207 | Hot stream outlet temperature | 5 | 126.800 C |
| E212 | Hot stream outlet temperature | 5C | 64.700 C |
| E215 | Hot stream outlet temperature | BENZENE | 38.300 C |
| E216 | Hot stream outlet temperature | TOLUENE | 44.700 C |
| E217 | Hot stream outlet temperature | XYLENE | 40.000 C |

Table 4.12 Specifications of splitters for extraction aromatic recovery unit

| Splitter | Stream | | Specification | |
|---|---|---|---|---|
| | Inlet | Outlets | Split fraction | Stream |
| S1 | 4 | 4A,4B | 0.9327 | 4A |
| S2 | 4B | 4C,4D | 0.5000 | 4C |
| S3 | 5 | 5A,6 | 0.8131 | 5A |
| S4 | 17 | 15,16 | 0.8269 | 16 |

ARU flowsheet consists of five recycle streams; 4, 5, 9, 10 and 15. Sensitivity analysis shows that recycle stream 5, 10 and 15 are not affected by the other recycle streams. While stream 4 and 9 affects each other. User defined convergence blocks are defined to converge these recycle streams. Since stream 4 and 9 affect one another they put together in a single user defined convergence block. Then we tried to simulate the integrated flowsheet with different convergence order but without success. Since recycle stream 5, 10 and 15 are independent they must be used to define user defined convergence block. Since recycle stream 4 and 9 are affected by one another, we start searching for other streams which affect stream 4 and 9. In can be easily seen from sensitivity analysis that stream 4 is directly affected by stream 7 and stream 9 is affected by 14. Now we used stream 7 and 14 instead of stream 4 and 9 to define user defined convergence block. Again we tried to simulate the integrated flowsheet with different convergence order. Convergence order can be easily determined from the simulation flowsheet. Finally integrated flowsheet was converged with the convergence order given below,

V201 P201
C-4
| C-3 S3
| | C-2 E202 E212 M3 C203 E203 V202 P204 S1 C201 E201 S2 M1 C202 P205
| | | M4 C205
| | (RETURN C-2)
| | F205 P206
| | C-1 C204 E205 V203 P209 S4
| | (RETURN C-1)
| | P207 E207
| (RETURN C-3)
| M5 P208
(RETURN C-4)
P210 V204 C207 P212 C208 E216 E217 E215 P203 M2

Where,

C-1: User defined convergence block used stream 15 as tear stream.

C-2: User defined convergence block used stream 7 and 14 as tear streams.

C-3: User defined convergence block used stream 5 as tear stream.

C-4: User defined convergence block used stream 10 as tear stream.

Broyden method is used for tear convergence. User defined convergence block input for C-2 and convergence order form are shown in Appendix B. Overall flowsheet balance of integrated flowsheet is given in Table 4.13.

Table 4.13 Overall Flowsheet balance for extraction aromatic recovery unit

| Mass and Energy balance | | | |
|---|---|---|---|
| | In | Out | Relative difference |
| Mole, kmol/sec | 6.32148 | 6.32148 | -0.543388E-07 |
| Mass, tonne/day | 10346.1 | 10346.1 | -0.968335E-06 |
| Enthalpy, Watt | -0.178406E+10 | -0.177634E+10 | -0.432380E-02 |

## 4.6 Validation

Before using simulation program of a flowsheet for troubleshooting, debottlenecking and other major purposes, it should be validated. The prime aim of validation of a simulation is to judge how well the simulation is reflecting the real world. A simulation that does not reflect the real world may result in a wrong diagnosis during troubleshooting. This may led to incorrect solutions.

### 4.6.1 Error Analysis

Simulation results are compared with plant data in terms of absolute error and relative percentage error.

$$\text{Absolute error} = \left|(\text{simulation result-plant data})\right| \tag{4.1}$$

$$\text{Relative percentage error} = \left[\frac{\left|(\text{simulation result-plant data})\right|}{\text{plant data}}\right] \times 100 \tag{4.2}$$

In some cases relative percentage error reflects large error even if the absolute error is not significant and vice versa. For example absolute error and relative percentage error for stream 14 is, respectively 2.4 MT/D and 27.907, where as for stream 2 is 15.921 MT/D and 5.789. Therefore both the errors have been used to analyze the simulation results. Comparison of simulation result with the plant data is given in Table 4.14.

Table 4.14 Comparison of simulation result with plant data

| Description | Unit | Plant value | Simulation tag number | Simulation result | Absolute error | Relative percentage error | Remarks |
|---|---|---|---|---|---|---|---|
| **B. Extraction Section (C201)** | | | | | | | |
| **1. Flow** | | | | | | | |
| Lean Solvent to extraction Column | MT/D | 1275.000 | 5A | 1275.007 | 0.007 | 0.001 | |
| Reflux to Extraction Column | MT/D | 155.300 | 4 | 156.515 | 1.215 | 0.782 | |
| Raffinate to wash column | MT/D | 275.000 | 2 | 259.079 | **15.921** | 5.789 | |
| Rich Solvent to Extract Stripper | MT/D | Faulty | 7A | 1811.901 | | | |
| **2. Temperature** | | | | | | | |
| Lean Solvent exit E202 | C | 101.400 | 5B | 100.500 | 0.900 | 0.888 | |
| **C. Raffinate wash column (C202)** | | | | | | | |
| **1. Flow** | | | | | | | |
| Water to RWC | MT/D | 20.700 | 10 | 20.700 | 0.000 | 0.000 | |
| Reflux | MT/D | Faulty | 3 | 262.730 | | | |
| Raffinate exit RWC | MT/D | 273.600 | NONARMTS | 268.001 | 5.599 | 2.046 | |
| **2. Temperatures** | | | | | | | |
| Raffinate to RWC | C | 40.800 | 2A+4C | 40.700 | 0.100 | 0.245 | |
| **D. Extract Stripper (C203)** | | | | | | | |
| **1. Flow** | | | | | | | |
| Lean Solvent to ES | MT/D | 384.200 | 6 | 293.076 | **91.124** | **23.718** | Faulty instrument |
| ES Top | MT/D | Faulty | 4+9 | 157.000 | | | |
| **2. Temperatures** | | | | | | | |
| ES Feed | C | 86.500 | 7A+6 | 85.500 | 1.000 | 1.156 | |
| Tray 38 | C | 103.400 | C203/2 | 101.463 | 1.937 | 1.873 | |
| Tray 16 | C | 122.100 | C203/24 | 113.451 | 8.649 | 7.084 | |
| Tray 1 | C | 122.700 | C203/39 | 125.277 | 2.577 | 2.100 | |
| ES bottom | C | 151.200 | 8A | 144.800 | 6.400 | 4.233 | |
| **E. Solvent Recovery Column (C204)** | | | | | | | |

*(continued on next page)*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1. Flows** | | | | | | | |
| SRC Feed | MT/D | 1936.000 | 8 | 1947.977 | **11.977** | 0.619 | |
| Reflux | MT/D | 80.000 | 15 | 79.981 | 0.019 | 0.024 | |
| Extract to Storage | MT/D | 375.000 | 16 | 382.078 | 7.078 | 1.887 | |
| **2. Temperatures** | | | | | | | |
| Top | C | 65.500 | UP204 | 66.900 | 1.400 | 2.137 | |
| Bottom | C | 129.800 | C204/34 | 126.041 | 3.759 | 2.896 | |
| **F. Water Stripper (C205)** | | | | | | | |
| **1. Flows** | | | | | | | |
| WS feed | MT/D | 51.200 | 11 | 33.804 | **17.396** | **33.977** | |
| WS top | MT/D | 8.600 | 14 | 11.000 | 2.400 | **27.907** | |
| Vapor to SRC | MT/D | Faulty | 12 | 8.442 | | | |
| **2. Temperatures** | | | | | | | |
| Vapors to SRC | C | 117.600 | 12 | 116.500 | 1.100 | 0.935 | |
| Lean solvent exit WS reboiler | C | 125.800 | 5 | 126.800 | 1.000 | 0.795 | |
| **H. Benzene Column (C207)** | | | | | | | |
| **1. Flows** | | | | | | | |
| Feed to benzene column | MT/D | 360.000 | 16A | 361.231 | 1.231 | 0.342 | |
| Benzene Drag | MT/D | 0.000 | 18 | 0.043 | 0.043 | | |
| **2. Temperatures** | | | | | | | |
| Top Temperature | C | 90.600 | C207/2 | 93.355 | 2.755 | 3.041 | |
| Bottom Temperature | C | 124.400 | C207/42 | 127.521 | 3.121 | 2.509 | |
| Draw tray temperature | C | 93.700 | C207/5 | 93.441 | 0.259 | 0.276 | |
| **I. Toluene Column (C208)** | | | | | | | |
| **1. Flows** | | | | | | | |
| Feed to Toluene Column | MT/D | 82.800 | 20A | 82.188 | 0.612 | 0.739 | |
| Toluene to Storage | MT/D | 80.000 | TOLUENE | 79.188 | 0.812 | 1.015 | |
| Toluene Column bottom to storage | MT/D | 3.000 | XYLENE | 3.000 | 0.000 | 0.000 | |
| **2. Temperatures** | | | | | | | |
| Top temperature | C | 117.500 | C208/2 | 118.824 | 1.324 | 1.127 | |
| Bottom Temperature | C | 136.200 | C208/50 | 131.536 | 4.664 | 3.424 | |

C203/2: 2nd tray from top ,of block C203

Section wise absolute error and relative percentage error ranges are respectively given in Table 4.15 and Table 4.16.

Table 4.15 Absolute error ranges for different sections

| | | Simulation tag number | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Extraction section | | | SR section | | Fractionation section | |
| Error range | Block ⟶ | C201 | C202 | C203 | C204 | C205 | C207 | C208 |
| < 1 | Flow, MT/D | 5A | 10 | | 15 | | 18 | 20A, TOLUENE, XYLENE |
| | Temperature, C | 5B | 2A+4C | | | | C207/5 | |
| 1 – 10 | Flow, MT/D | 4 | NONARMTS | | 16 | 14 | 16A | |
| | Temperature, C | | | 7A+6, 8A, C203/2, C203/24, C203/39 | UP204, C204/34 | 12, 5 | C207/2, C207/42 | C208/2, C208/50 |
| 10 – 20 | Flow, MT/D | 2 | | | 8 | 11 | | |
| | Temperature, C | | | | | | | |
| 20 – 100 | Flow, MT/D | | | 6 | | | | |
| | Temperature, C | | | | | | | |

Table 4.16 Relative percentage error ranges for different sections

| | | Simulation tag number | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Extraction section | | | SR section | | Fractionation section | |
| Error range | Block ⟶ | C201 | C202 | C203 | C204 | C205 | C207 | C208 |
| < 1 % | Flow | 5A, 4 | 10 | | 8, 15 | | 16A | 20A, XYLENE |
| | Temperature | 5B | 2A+4C | | | 12, 5 | C207/5 | |
| (1 – 10) % | Flow | 2 | NONARMTS | | 16 | | | TOLUENE |
| | Temperature | | | 7A+6, 8A, C203/2, C203/24, C203/39 | UP204, C204/34 | | C207/2, C207/42 | C208/2, C208/50 |
| (10 – 50) % | Flow | | | 6 | | 11, 14 | | |
| | Temperature | | | | | | | |

Absolute error for stream 6, 8, and 11 are more than 10, with stream 6 having highest absolute error of 91.124 MT/D, where as absolute percentage error for stream 6, 11 and 14 are greater than 10. Absolute error for stream 6 is too high, which is not permissible. Therefore we have done the mass balance across solvent recovery column and water stripper.

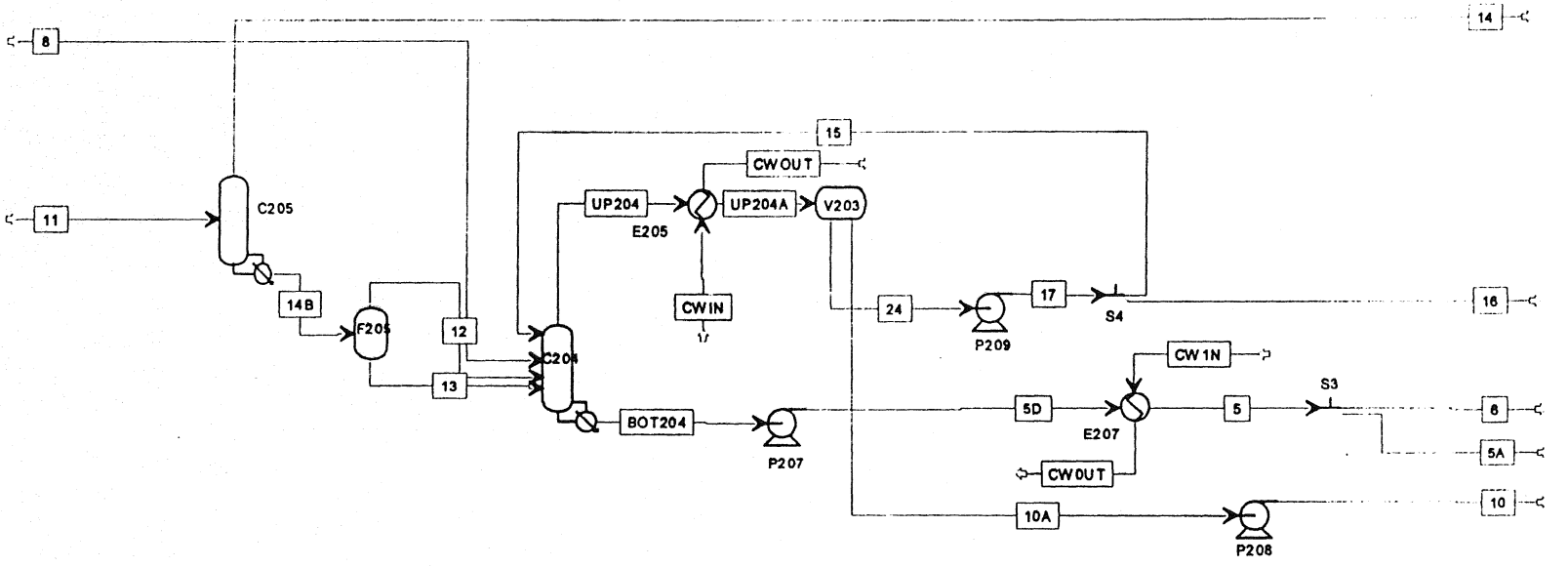


Figure 4.1 Input and output streams for combined solvent recovery column and extract stripper

Table 4.17 Mass balances across solvent recovery column and extract stripper

| Input | | Output | |
|---|---|---|---|
| Stream | Plant data, MT/D | Stream | Plant Data |
| 8 | 1936.000 | 14 | 8.600 |
| 11 | 51.200 | 16 | 375.000 |
| | | 6 | X |
| | | 5A | 1275.000 |
| | | 10 | 20.700 |
| Total, MT/D | 1987.200 | Total, MT/D | 1679.300+X |
| | | Value of stream 6, X=(1987.200-1679.300)=307.900 | |

Input and output streams for combined solvent recovery column and extract stripper are shown in Figure 4.1. Mass balance across these two columns is shown in Table 4.17. It is found that actual value of stream 6 flow rate could be 307.900 MT/D as compared to 384.200 MT/D of given data. This is may be due to faulty flow rate measurement instrument. Therefore we marked it as faulty instrument. For further calculations we used the calculated value of stream 6 flow rate, 307.900 MT/D, instead of given data. Since stream 6, 8, 11, and 14 associated with high error, absolute error or relative percentage error, these streams must be considered for error minimization.

### 4.6.2 Sensitivity Analysis

To investigate the other possible stream flow rates affected by stream flow rates of 6, 8, 11, and 14, and to get the manipulated variables which affects theses stream flow rates, we have done the sensitivity analysis with respect to different variables. It is found that distillate rate of C203, boilup ratio of C204 and C205 are most responsible manipulated variable for variation of these stream flow rates. Effect of C203 distillate rate is shown in Figure 4.2.

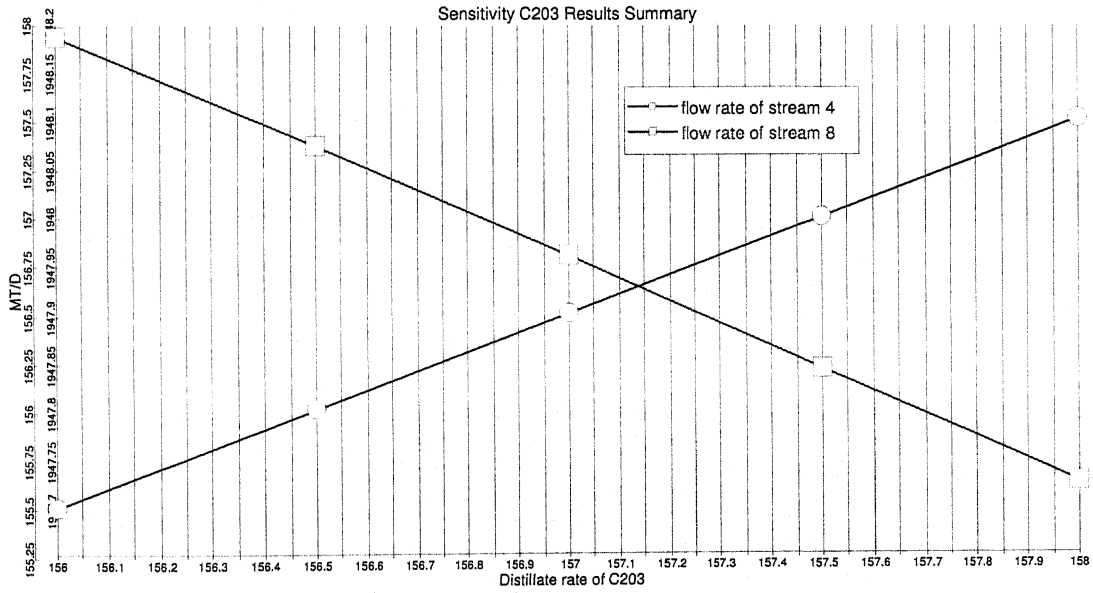


Figure 4.2 Effect of distillate rate of C203.

Flow rates of stream 4 and 8 are affected by distillate rate of C203. Hence, flow rate of stream 4 must be taken into account while error minimization by optimization. Effect of boilup ratio of C204 and C205 is respectively shown in Figure 4.3 and 4.4.

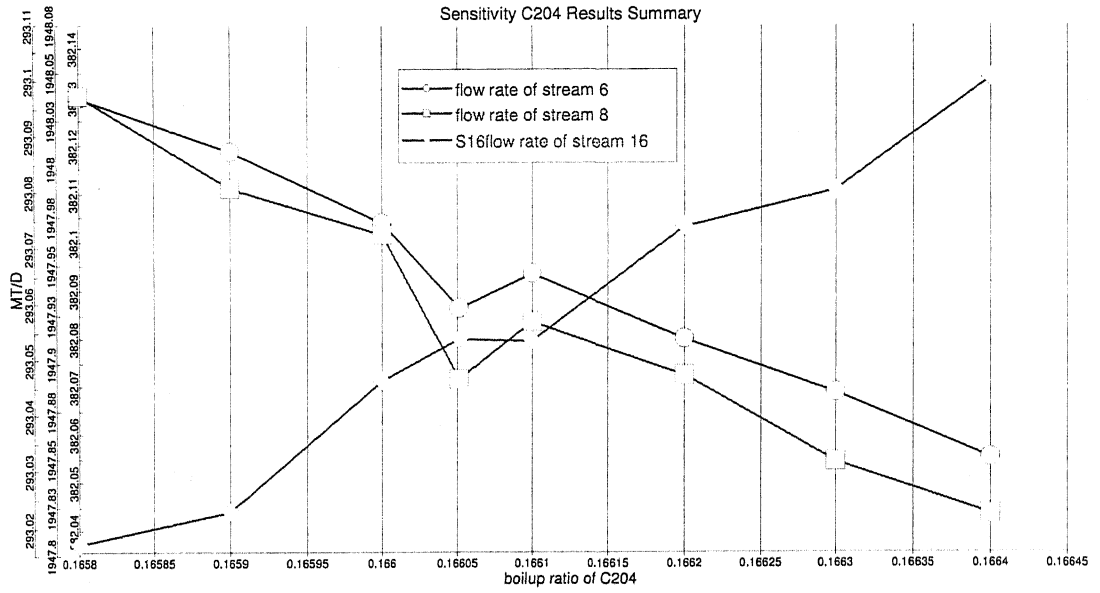


Figure 4.3 Effect of boilup ratio of C204.

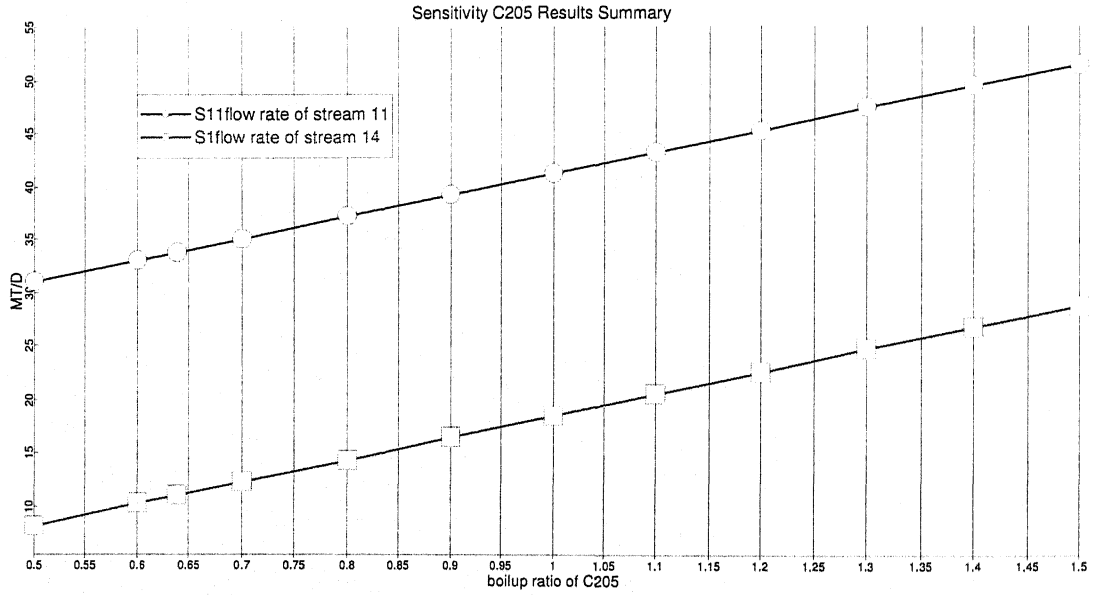


Figure 4.4 Effect of boilup ratio of C205.

The other stream flow rate which is affected by boilup ratio of C203 is flow rate of stream 16. Thus, flow rate of stream 4, 6, 8, 11, 14 and 16 are considered for error minimization by optimization.

Sensitivity parameter $s$ can be defined as,

$$s_{ij} = \left| \left( \frac{\partial y_i}{\partial x_j} \right) \times \left( \frac{x_j}{y_i} \right) \right| \text{ at operating point} \qquad (4.3)$$

Where, $x_j$ and $y_i$ are respectively manipulated variables and dependent variables. Sensitivity parameters for same stream flow rate and different manipulated variable are added to get sensitivity index, $W_i$. Sensitivity parameter and sensitivity index for different dependent variables are given in Table 4.18. These sensitivity indexes are used in error minimization by optimization.

Table 4.18 Sensitivity parameter and sensitivity index for extraction aromatic recovery unit

| Manipulated variable | | Dependent variable | | | | | |
|---|---|---|---|---|---|---|---|
| | | 4 | 6 | 8 | 11 | 14 | 16 |
| | | Flow, MT/D | Flow, MT/D | Flow, MT/D | Flow, MT/D | Flow, MT/D | Flow, MT/D |
| Block | Variable | $s_{1j}$ | $s_{2j}$ | $s_{3j}$ | $s_{4j}$ | $s_{5j}$ | $s_{6j}$ |
| C203 | Distillate rate, MT/D | 1.0054 | 0.0136 | 0.0186 | 0.0162 | 0.0021 | 0.0392 |
| C204 | Boilup ratio, mole | 0.0447 | 0.0607 | 0.0307 | 0.3438 | 0.3181 | 0.0701 |
| C205 | Boilup ratio, mole | 0.0007 | 0.0000 | 0.0000 | 0.3844 | 1.1903 | 0.0000 |
| Sensitivity index, $W_i = \sum S_{ij}$ ⟶ | | 1.0507 | 0.0743 | 0.0494 | 0.7444 | 1.5105 | 0.1093 |

### 4.6.3 Error minimization

Optimization tool in ASPEN PLUS is used to minimize the gap between plant data and the simulation results. An objective function $F$ is formulated and minimized using optimization tool.

$$F = \sum W_i \times \left( \frac{plant\ data_i - simulated\ data_i}{plant\ data_i} \right)^2 \qquad (4.4)$$

For our case the objective function, OED used for minimizing the gap between the flow rate of stream 4, 6, 8, 11, 14 and 16 and the respective plant data is as follows:

O1=1.050746009*((155.300-F4)/155.300)*((155.300-F4)/155.300)

O2=0.074303828*((307.900-F6)/307.900)*((307.900-F6)/307.900)

O3=0.049359673*((1936.000-F8)/1936.000)*((1936.000-F8)/1936.000)

O4=0.744412593*((51.200-F11)/51.2)*((51.200-F11)/51.2)

O5=1.510530204*((8.600-F14)/8.600)*((8.600-F14)/8.600)

O6=0.109332429*((375.000-F16)/375.000)*((375.000-F16)/375.000)

OED=O1+O2+O3+O4+O5+O6

Where F stands for flow rate and the number following F is stream number, for example F4 is the flow rate of stream 4. Final values of manipulated variables are given in Table 4.19.

Table 4.19 Manipulated variables after error minimization for extraction aromatic recovery unit

| Manipulated variable | | | | |
|---|---|---|---|---|
| Block | Variable | Limits | | Final value |
| | | Lower | Upper | |
| Extraction and Solvent recovery section | | | | |
| C203 | Distillate rate, MT/D | 156.0000 | 158.0000 | 156.9389 |
| C204 | Boilup ratio, mole | 0.1658 | 0.1664 | 0.1661 |
| C205 | Boilup ratio, mole | 0.5000 | 1.5000 | 0.5379 |

Comparison of simulation result and plant data after error minimization is given in Table 4.20. Even after the error minimization both absolute error and relative percentage error for flow rate of stream 11 is too high. This is may be due to the faulty flow rate measuring instrument. Therefore we marked it as faulty instrument. Stream results after error minimization is given in Table 4.21. End products purity is given in Table 4.22.

Table 4.22 Products purity for extraction aromatic recovery unit

| Description | Stream | Simulation result |
|---|---|---|
| Aromatics in non aromatics product | NONARMTS | 3.900 % |
| Non aromatics in benzene product | BENZENE | 3.750 PPM |
| Toluene in benzene product | BENZENE | **214.000 PPM** |
| Benzene in toluene product | TOLUENE | **257.000 PPM** |

Table 4.20 Comparison of simulation result with plant data after error minimization

| Description | Unit | Plant value | Simulation tag number | Simulation result | Absolute error | Relative percentage error | Remarks |
|---|---|---|---|---|---|---|---|
| **B. Extraction Section (C201)** | | | | | | | |
| **1. Flow** | | | | | | | |
| Lean Solvent to extraction Column | MT/D | 1275.000 | 5A | 1275.000 | 0.000 | 0.000 | |
| Reflux to Extraction Column | MT/D | 155.300 | 4 | 156.426 | 1.126 | 0.725 | |
| Raffinate to wash column | MT/D | 275.000 | 2 | 259.081 | **15.919** | 5.789 | |
| Rich Solvent to Extract Stripper | MT/D | Faulty | 7A | 1811.802 | | | |
| **2. Temperature** | | | | | | | |
| Lean Solvent exit E202 | C | 101.400 | 5B | 100.500 | 0.900 | 0.888 | |
| **C. Raffinate wash column (C202)** | | | | | | | |
| **1. Flow** | | | | | | | |
| Water to RWC | MT/D | 20.700 | 10 | 20.701 | 0.001 | 0.005 | |
| Reflux | MT/D | Faulty | 3 | 262.730 | | | |
| Raffinate exit RWC | MT/D | 273.600 | NONARMTS | 267.997 | 5.603 | 2.048 | |
| **2. Temperatures** | | | | | | | |
| Raffinate to RWC | C | 40.800 | 2A+4C | 40.700 | 0.100 | 0.245 | |
| **D. Extract Stripper (C203)** | | | | | | | |
| **1. Flow** | | | | | | | |
| Lean Solvent to ES | MT/D | 307.900 | 6 | 292.870 | **15.030** | 4.881 | Faulty instrument |
| ES Top | MT/D | Faulty | 4+9 | 156.939 | | | |
| **2. Temperatures** | | | | | | | |
| ES Feed | C | 86.500 | 7A+6 | 85.500 | 1.000 | 1.156 | |
| Tray 38 | C | 103.400 | C203/2 | 101.458 | 1.942 | 1.878 | |
| Tray 16 | C | 122.100 | C203/24 | 113.439 | 8.661 | 7.093 | |
| Tray 1 | C | 122.700 | C203/39 | 125.274 | 2.574 | 2.098 | |
| ES bottom | C | 151.200 | 8A | 144.800 | 6.400 | 4.233 | |
| **E. Solvent Recovery Column (C204)** | | | | | | | |

*(continued on next page)*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **1. Flows** | | | | | | | |
| SRC Feed | MT/D | 1936.000 | 8 | 1947.734 | **11.734** | 0.606 | |
| Reflux | MT/D | 80.000 | 15 | 79.980 | 0.020 | 0.025 | |
| Extract to Storage | MT/D | 375.000 | 16 | 382.075 | 7.075 | 1.887 | |
| **2. Temperatures** | | | | | | | |
| Top | C | 65.500 | UP204 | 66.900 | 1.400 | 2.137 | |
| Bottom | C | 129.800 | C204/34 | 126.030 | 3.770 | 2.904 | |
| **F. Water Stripper (C205)** | | | | | | | |
| **1. Flows** | | | | | | | |
| WS feed | MT/D | 51.200 | 11 | 31.772 | **19.428** | **37.945** | Faulty instrument |
| WS top | MT/D | 8.600 | 14 | 8.940 | 0.340 | 3.953 | |
| Vapor to SRC | MT/D | Faulty | 12 | 8.444 | | | |
| **2. Temperatures** | | | | | | | |
| Vapors to SRC | C | 117.600 | 12 | 116.500 | 1.100 | 0.935 | |
| Lean solvent exit WS reboiler | C | 125.800 | 5 | 126.800 | 1.000 | 0.795 | |
| **H. Benzene Column (C207)** | | | | | | | |
| **1. Flows** | | | | | | | |
| Feed to benzene column | MT/D | 360.000 | 16A | 361.227 | 1.227 | 0.341 | |
| Benzene Drag | MT/D | 0.000 | 18 | 0.040 | 0.040 | | |
| **2. Temperatures** | | | | | | | |
| Top Temperature | C | 90.600 | C207/2 | 93.355 | 2.755 | 3.041 | |
| Bottom Temperature | C | 124.400 | C207/42 | 127.519 | 3.119 | 2.507 | |
| Draw tray temperature | C | 93.700 | C207/5 | 93.440 | 0.260 | 0.277 | |
| **I. Toluene Column (C208)** | | | | | | | |
| **1. Flows** | | | | | | | |
| Feed to Toluene Column | MT/D | 82.800 | 20A | 82.187 | 0.613 | 0.740 | |
| Toluene to Storage | MT/D | 80.000 | TOLUENE | 79.187 | 0.813 | 1.016 | |
| Toluene Column bottom to storage | MT/D | 3.000 | XYLENE | 3.000 | 0.000 | 0.000 | |
| **2. Temperatures** | | | | | | | |
| Top temperature | C | 117.500 | C208/2 | 118.823 | 1.323 | 1.126 | |
| Bottom Temperature | C | 136.200 | C208/50 | 131.526 | 4.674 | 3.432 | |

Table 4.21 Simulation stream results for extraction aromatic recovery unit

| Stream | 1 | 2 | 2A | 2A+4C | 3 | 3A | 4 | 4+9 |
|---|---|---|---|---|---|---|---|---|
| To | P201 | E201 | M1 | C202 | M2 | P203 | S1 | V202 |
| From | V201 | C201 | E201 | M1 | P203 | C202 | P204 | E203 |
| State | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID |
| Mass Flow tonne/day | | | | | | | | |
| n-Pentane | 29.720 | 28.647 | 28.647 | 29.185 | 29.182 | 29.182 | 15.984 | 15.981 |
| n-Hexane | 54.940 | 53.908 | 53.908 | 54.422 | 54.420 | 54.420 | 15.267 | 15.265 |
| Iso-Pentane | 25.840 | 24.902 | 24.902 | 25.372 | 25.369 | 25.369 | 13.987 | 13.984 |
| 2-Methyl pentane | 130.180 | 127.732 | 127.732 | 128.958 | 128.954 | 128.954 | 36.428 | 36.423 |
| Cis-2-Hexene | 6.790 | 5.095 | 5.095 | 5.594 | 5.590 | 5.590 | 14.826 | 14.822 |
| Methylcyclopentane | 13.450 | 10.631 | 10.631 | 10.675 | 10.674 | 10.674 | 1.307 | 1.306 |
| Benzene | 299.970 | 0.082 | 0.082 | 1.819 | 1.818 | 1.818 | 51.584 | 51.583 |
| Toluene | 85.820 | 4.548 | 4.548 | 4.767 | 4.767 | 4.767 | 6.496 | 6.496 |
| *o*-Xylene | 3.290 | 1.891 | 1.891 | 1.894 | 1.894 | 1.894 | 0.086 | 0.085 |
| Sulfolane | 0.000 | 1.643 | 1.643 | 1.656 | 0.000 | 0.000 | 0.380 | 0.160 |
| water | 0.000 | 0.004 | 0.004 | 0.006 | 0.063 | 0.063 | 0.081 | 0.833 |
| Total Flow kmol/sec | 0.0921 | 0.0361 | 0.0361 | 0.0369 | 0.0367 | 0.0367 | 0.0225 | 0.0230 |
| Total Flow tonne/day | 650.000 | 259.081 | 259.081 | 264.349 | 262.730 | 262.730 | 156.426 | 156.939 |
| Total Flow cum/sec | 9.975E-03 | 5.003E-03 | 4.657E-03 | 4.741E-03 | 4.724E-03 | 4.723E-03 | 2.577E-03 | 2.683E-03 |
| Temperature C | 39.964 | 83.200 | 40.800 | 40.661 | 40.181 | 40.000 | 40.305 | 66.900 |
| Pressure kg/sqcm | 1.982 | 6.023 | 6.023 | 5.000 | 5.000 | 3.080 | 5.000 | 1.488 |
| Vapor Frac | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Liquid Frac | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Enthalpy J/kg | -5.891E+05 | -2.121E+06 | -2.227E+06 | -2.205E+06 | -2.200E+06 | -2.201E+06 | -1.126E+06 | -1.129E+06 |
| Enthalpy Watt | -4.432E+06 | -6.360E+06 | -6.677E+06 | -6.745E+06 | -6.691E+06 | -6.692E+06 | -2.039E+06 | -2.050E+06 |
| Entropy J/kg-K | -4784.172 | -6861.041 | -7174.453 | -7139.254 | -7161.192 | -7162.094 | -5580.711 | -5400.957 |
| Density kg/cum | 754.238 | 599.426 | 643.955 | 645.301 | 643.654 | 643.835 | 702.585 | 676.940 |
| Average MW | 81.645 | 83.069 | 83.069 | 83.014 | 82.788 | 82.788 | 80.371 | 79.023 |
| Liq Vol 60F cum/sec | 9.723E-03 | 4.536E-03 | 4.536E-03 | 4.620E-03 | 4.605E-03 | 4.605E-03 | 2.501E-03 | 2.507E-03 |

*(continued on next page)*

| Stream | 4A | 4B | 4C | 4D | 4E | 4P9 | .5 | 5A |
|---|---|---|---|---|---|---|---|---|
| To | C201 | S2 | M1 | M2 | P204 | E203 | S3 | E202 |
| From | S1 | S1 | S2 | S2 | V202 | C203 | E207 | S3 |
| State | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | VAPOR | LIQUID | LIQUID |
| Mass Flow tonne/day | | | | | | | | |
| n-Pentane | 14.908 | 1.076 | 0.538 | 0.538 | 15.984 | 15.981 | 0.000 | 0.000 |
| n-Hexane | 14.239 | 1.028 | 0.514 | 0.514 | 15.267 | 15.265 | 0.000 | 0.000 |
| Iso-Pentane | 13.045 | 0.942 | 0.471 | 0.471 | 13.987 | 13.984 | 0.000 | 0.000 |
| 2-Methyl pentane | 33.975 | 2.453 | 1.227 | 1.227 | 36.428 | 36.423 | 0.000 | 0.000 |
| Cis-2-Hexene | 13.827 | 0.998 | 0.499 | 0.499 | 14.826 | 14.822 | 0.000 | 0.000 |
| Methylcyclopentane | 1.219 | 0.088 | 0.044 | 0.044 | 1.307 | 1.306 | 0.000 | 0.000 |
| Benzene | 48.110 | 3.474 | 1.737 | 1.737 | 51.584 | 51.583 | 0.241 | 0.196 |
| Toluene | 6.059 | 0.437 | 0.219 | 0.219 | 6.496 | 6.496 | 7.789 | 6.333 |
| *o*-Xylene | 0.080 | 0.006 | 0.003 | 0.003 | 0.086 | 0.085 | 1.825 | 1.484 |
| Sulfolane | 0.355 | 0.026 | 0.013 | 0.013 | 0.380 | 0.160 | 1554.846 | 1264.419 |
| water | 0.075 | 0.005 | 0.003 | 0.003 | 0.081 | 0.833 | 3.156 | 2.567 |
| Total Flow kmol/sec | 0.0210 | 0.0015 | 0.0008 | 0.0008 | 0.0225 | 0.0230 | 0.1530 | 0.1244 |
| Total Flow tonne/day | 145.891 | 10.535 | 5.267 | 5.267 | 156.426 | 156.939 | 1567.858 | 1275.000 |
| Total Flow cum/sec | 2.403E-03 | 1.735E-04 | 8.677E-05 | 8.677E-05 | 2.576E-03 | 4.692E-01 | 1.553E-02 | 1.263E-02 |
| Temperature C | 40.305 | 40.305 | 40.305 | 40.305 | 40.000 | 98.965 | 126.800 | 126.800 |
| Pressure kg/sqcm | 5.000 | 5.000 | 5.000 | 5.000 | 2.521 | 1.488 | 5.000 | 5.000 |
| Vapor Frac | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 1.000 | 0.000 | 0.000 |
| Liquid Frac | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 0.000 | 1.000 | 1.000 |
| Enthalpy J/kg | -1.126E+06 | -1.126E+06 | -1.126E+06 | -1.126E+06 | -1.127E+06 | -7.151E+05 | -3.511E+06 | -3.511E+06 |
| Enthalpy Watt | -1.902E+06 | -1.373E+05 | -6.865E+04 | -6.865E+04 | -2.040E+06 | -1.299E+06 | -6.371E+07 | -5.181E+07 |
| Entropy J/kg-K | -5580.711 | -5580.711 | -5580.711 | -5580.711 | -5582.289 | -4211.790 | -4240.265 | -4240.262 |
| Density kg/cum | 702.585 | 702.585 | 702.585 | 702.585 | 702.892 | 3.871 | 1168.321 | 1168.319 |
| Average MW | 80.371 | 80.371 | 80.371 | 80.371 | 80.371 | 79.023 | 118.611 | 118.611 |
| Liq Vol 60F cum/sec | 2.332E-03 | 1.684E-04 | 8.420E-05 | 8.420E-05 | 2.501E-03 | 2.507E-03 | 1.443E-02 | 1.174E-02 |

*(continued on next page)*

| Stream | 5B | 5C | 5D | 6 | 7 | 7A | 7A+6 | 8 |
|---|---|---|---|---|---|---|---|---|
| To | E212 | C201 | E207 | M3 | E202 | M3 | C203 | C204 |
| From | E202 | E212 | P207 | S3 | C201 | E202 | M3 | P206 |
| State | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID |
| Mass Flow tonne/day | | | | | | | | |
| n-Pentane | 0.000 | 0.000 | 0.000 | 0.000 | 15.981 | 15.981 | 15.981 | 0.000 |
| n-Hexane | 0.000 | 0.000 | 0.000 | 0.000 | 15.271 | 15.271 | 15.271 | 0.006 |
| Iso-Pentane | 0.000 | 0.000 | 0.000 | 0.000 | 13.984 | 13.984 | 13.984 | 0.000 |
| 2-Methyl pentane | 0.000 | 0.000 | 0.000 | 0.000 | 36.423 | 36.423 | 36.423 | 0.000 |
| Cis-2-Hexene | 0.000 | 0.000 | 0.000 | 0.000 | 15.520 | 15.520 | 15.520 | 0.699 |
| Methylcyclopentane | 0.000 | 0.000 | 0.000 | 0.000 | 4.038 | 4.038 | 4.038 | 2.732 |
| Benzene | 0.196 | 0.196 | 0.241 | 0.045 | 348.190 | 348.190 | 348.235 | 296.651 |
| Toluene | 6.333 | 6.333 | 7.789 | 1.455 | 93.663 | 93.663 | 95.117 | 88.622 |
| *o*-Xylene | 1.484 | 1.484 | 1.825 | 0.341 | 2.963 | 2.963 | 3.304 | 3.219 |
| Sulfolane | 1264.419 | 1264.419 | 1554.846 | 290.440 | 1263.131 | 1263.131 | 1553.571 | 1553.411 |
| water | 2.567 | 2.567 | 3.156 | 0.590 | 2.638 | 2.638 | 3.228 | 2.395 |
| Total Flow kmol/sec | 0.1244 | 0.1244 | 0.1530 | 0.0286 | 0.2015 | 0.2015 | 0.2300 | 0.2071 |
| Total Flow tonne/day | 1275.000 | 1275.000 | 1567.858 | 292.870 | 1811.802 | 1811.802 | 2104.673 | 1947.734 |
| Total Flow cum/sec | 1.239E-02 | 1.208E-02 | 1.660E-02 | 2.901E-03 | 1.995E-02 | 2.026E-02 | 2.318E-02 | 2.148E-02 |
| Temperature C | 100.511 | 64.700 | 208.754 | 126.800 | 61.200 | 79.300 | 85.483 | 138.205 |
| Pressure kg/sqcm | 5.000 | 5.000 | 5.000 | 5.000 | 9.083 | 9.083 | 5.000 | 6.033 |
| Vapor Frac | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Liquid Frac | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Enthalpy J/kg | -3.554E+06 | -3.608E+06 | -3.365E+06 | -3.511E+06 | -2.508E+06 | -2.478E+06 | -2.622E+06 | -2.657E+06 |
| Enthalpy Watt | -5.244E+07 | -5.324E+07 | -6.106E+07 | -1.190E+07 | -5.258E+07 | -5.196E+07 | -6.386E+07 | -5.991E+07 |
| Entropy J/kg-K | -4348.302 | -4496.379 | -3909.527 | -4240.262 | -4244.299 | -4159.727 | -4165.657 | -3857.178 |
| Density kg/cum | 1191.312 | 1221.892 | 1093.134 | 1168.319 | 1051.167 | 1035.100 | 1050.779 | 1049.537 |
| Average MW | 118.611 | 118.611 | 118.611 | 118.611 | 104.085 | 104.085 | 105.890 | 108.872 |
| Liq Vol 60F cum/sec | 1.174E-02 | 1.174E-02 | 1.443E-02 | 2.696E-03 | 1.926E-02 | 1.926E-02 | 2.195E-02 | 1.945E-02 |

(*continued on next page*)

| Stream | 8A | 9 | 10 | 10A | 11 | 11A | 11B | 12 |
|---|---|---|---|---|---|---|---|---|
| To | P206 | P205 | C202 | M5 | C205 | M4 | M4 | C204 |
| From | C203 | V202 | P208 | V203 | M4 | C202 | P205 | F205 |
| State | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | VAPOR |
| Mass Flow tonne/day | | | | | | | | |
| n-Pentane | 0.000 | 0.001 | 0.000 | 0.000 | 0.005 | 0.004 | 0.001 | 0.000 |
| n-Hexane | 0.006 | 0.000 | 0.000 | 0.000 | 0.002 | 0.002 | 0.000 | 0.000 |
| Iso-Pentane | 0.000 | 0.001 | 0.000 | 0.000 | 0.004 | 0.003 | 0.001 | 0.000 |
| 2-Methyl pentane | 0.000 | 0.001 | 0.000 | 0.000 | 0.006 | 0.005 | 0.001 | 0.000 |
| Cis-2-Hexene | 0.699 | 0.005 | 0.000 | 0.000 | 0.009 | 0.004 | 0.005 | 0.000 |
| Methylcyclopentane | 2.732 | 0.000 | 0.000 | 0.000 | 0.001 | 0.001 | 0.000 | 0.000 |
| Benzene | 296.651 | 0.008 | 0.000 | 0.000 | 0.008 | 0.001 | 0.008 | 0.000 |
| Toluene | 88.622 | 0.000 | 0.000 | 0.000 | 0.001 | 0.000 | 0.000 | 0.000 |
| *o*-Xylene | 3.219 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Sulfolane | 1553.411 | 0.258 | 0.000 | 0.000 | 1.914 | 1.656 | 0.258 | 0.019 |
| water | 2.395 | 9.179 | 20.701 | 20.632 | 29.822 | 20.644 | 9.179 | 8.426 |
| Total Flow kmol/sec | 0.2071 | 0.0059 | 0.0133 | 0.0133 | 0.0193 | 0.0134 | 0.0059 | 0.0054 |
| Total Flow tonne/day | 1947.734 | 9.454 | 20.701 | 20.632 | 31.772 | 22.319 | 9.454 | 8.444 |
| Total Flow cum/sec | 2.161E-02 | 1.114E-04 | 2.448E-04 | 2.439E-04 | 3.729E-04 | 2.615E-04 | 1.114E-04 | 9.921E-02 |
| Temperature C | 144.822 | 40.000 | 40.056 | 40.000 | 41.472 | 42.000 | 40.262 | 116.499 |
| Pressure kg/sqcm | 1.700 | 2.521 | 2.500 | 1.500 | 6.480 | 6.480 | 6.500 | 1.783 |
| Vapor Frac | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 1.000 |
| Liquid Frac | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 0.000 |
| Enthalpy J/kg | -2.658E+06 | -1.544E+07 | -1.580E+07 | -1.580E+07 | -1.504E+07 | -1.488E+07 | -1.544E+07 | -1.323E+07 |
| Enthalpy Watt | -5.992E+07 | -1.689E+06 | -3.785E+06 | -3.773E+06 | -5.532E+06 | -3.843E+06 | -1.689E+06 | -1.293E+06 |
| Entropy J/kg-K | -3851.059 | -8709.524 | -8840.321 | -8840.965 | -8550.271 | -8484.575 | -8706.509 | -2220.953 |
| Density kg/cum | 1043.383 | 982.558 | 978.879 | 978.933 | 986.203 | 987.893 | 982.300 | 0.985 |
| Average MW | 108.872 | 18.470 | 18.015 | 18.015 | 19.005 | 19.242 | 18.470 | 18.049 |
| Liq Vol 60F cum/sec | 1.945E-02 | 1.091E-04 | 2.401E-04 | 2.393E-04 | 3.640E-04 | 2.549E-04 | 1.091E-04 | 9.788E-05 |

(*continued on next page*)

| Stream | 13 | 14 | 14B | 15 | 16 | 16A | 17 | 18 |
|---|---|---|---|---|---|---|---|---|
| To | C204 | V202 | F205 | C204 | P210 | C207 | S4 | |
| From | F205 | C205 | C205 | S4 | S4 | V204 | P209 | C207 |
| State | LIQUID | VAPOR | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID |
| Mass Flow tonne/day | | | | | | | | |
| n-Pentane | 0.000 | 0.005 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| n-Hexane | 0.000 | 0.002 | 0.000 | 0.001 | 0.006 | 0.000 | 0.007 | 0.000 |
| Iso-Pentane | 0.000 | 0.004 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 2-Methyl pentane | 0.000 | 0.006 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Cis-2-Hexene | 0.000 | 0.009 | 0.000 | 0.146 | 0.699 | 0.000 | 0.845 | 0.000 |
| Methylcyclopentane | 0.000 | 0.001 | 0.000 | 0.572 | 2.732 | 0.001 | 3.304 | 0.000 |
| Benzene | 0.000 | 0.008 | 0.000 | 62.048 | 296.410 | 279.000 | 358.458 | 0.040 |
| Toluene | 0.000 | 0.001 | 0.000 | 16.921 | 80.833 | 80.833 | 97.754 | 0.000 |
| *o*-Xylene | 0.000 | 0.000 | 0.000 | 0.292 | 1.393 | 1.393 | 1.685 | 0.000 |
| Sulfolane | 1.417 | 0.479 | 1.435 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| water | 12.971 | 8.426 | 21.396 | 0.001 | 0.003 | 0.000 | 0.003 | 0.000 |
| Total Flow kmol/sec | 0.0085 | 0.0055 | 0.0139 | 0.0115 | 0.0547 | 0.0516 | 0.0661 | 0.0000 |
| Total Flow tonne/day | 14.387 | 8.940 | 22.832 | 79.980 | 382.075 | 361.227 | 462.056 | 0.040 |
| Total Flow cum/sec | 1.820E-04 | 1.003E-01 | 2.914E-04 | 1.084E-03 | 5.178E-03 | 5.310E-03 | 6.262E-03 | 5.831E-07 |
| Temperature C | 116.499 | 118.305 | 118.838 | 40.009 | 40.009 | 104.100 | 40.009 | 93.328 |
| Pressure kg/sqcm | 1.783 | 1.783 | 1.813 | 1.610 | 1.610 | 12.773 | 1.610 | 1.503 |
| Vapor Frac | 0.000 | 1.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Liquid Frac | 1.000 | 0.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Enthalpy J/kg | -1.430E+07 | -1.266E+07 | -1.480E+07 | 5.263E+05 | 5.263E+05 | 6.619E+05 | 5.263E+05 | 7.500E+05 |
| Enthalpy Watt | -2.381E+06 | -1.310E+06 | -3.911E+06 | 4.872E+05 | 2.327E+06 | 2.767E+06 | 2.814E+06 | 3.504E+02 |
| Entropy J/kg-K | -7546.892 | -2259.168 | -7854.530 | -3230.351 | -3230.351 | -2859.356 | -3230.351 | -2867.958 |
| Density kg/cum | 914.888 | 1.031 | 906.792 | 854.035 | 854.035 | 787.410 | 854.035 | 801.249 |
| Average MW | 19.661 | 18.936 | 19.032 | 80.846 | 80.846 | 80.954 | 80.846 | 78.114 |
| Liq Vol 60F cum/sec | 1.634E-04 | 1.027E-04 | 2.613E-04 | 1.054E-03 | 5.035E-03 | 4.753E-03 | 6.089E-03 | 5.294E-07 |

*(continued on next page)*

| Stream | 19 | 20 | 20A | 22 | 23 | 24 | 36 | 37 |
|---|---|---|---|---|---|---|---|---|
| To | E215 | P212 | C208 | E216 | E217 | P209 | | E215 |
| From | C207 | C207 | P212 | C208 | C208 | V203 | E215 | |
| State | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID |
| Mass Flow tonne/day | | | | | | | | |
| n-Pentane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| n-Hexane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.007 | 0.000 | 0.000 |
| Iso-Pentane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 2-Methyl pentane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Cis-2-Hexene | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.845 | 0.000 | 0.000 |
| Methylcyclopentane | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 3.304 | 0.000 | 0.000 |
| Benzene | 278.939 | 0.020 | 0.020 | 0.020 | 0.000 | 358.458 | 0.000 | 0.000 |
| Toluene | 0.060 | 80.773 | 80.773 | 79.162 | 1.612 | 97.754 | 0.000 | 0.000 |
| *o*-Xylene | 0.000 | 1.393 | 1.393 | 0.005 | 1.388 | 1.685 | 0.000 | 0.000 |
| Sulfolane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| water | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.003 | 350.000 | 350.000 |
| Total Flow kmol/sec | 0.0413 | 0.0103 | 0.0103 | 0.0099 | 0.0004 | 0.0661 | 0.2249 | 0.2249 |
| Total Flow tonne/day | 279.000 | 82.187 | 82.187 | 79.187 | 3.000 | 462.056 | 350.000 | 350.000 |
| Total Flow cum/sec | 4.031E-03 | 1.250E-03 | 1.245E-03 | 1.190E-03 | 4.515E-05 | 6.262E-03 | 4.158E-03 | 4.077E-03 |
| Temperature C | 93.440 | 127.738 | 125.192 | 118.780 | 131.526 | 40.000 | 44.816 | 25.000 |
| Pressure kg/sqcm | 1.508 | 1.552 | 7.033 | 1.233 | 1.289 | 1.500 | 1.033 | 1.033 |
| Vapor Frac | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Liquid Frac | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Enthalpy J/kg | 7.501E+05 | 3.144E+05 | 3.167E+05 | 3.019E+05 | 1.637E+05 | 5.262E+05 | -1.578E+07 | -1.586E+07 |
| Enthalpy Watt | 2.422E+06 | 2.990E+05 | 3.013E+05 | 2.767E+05 | 5.684E+03 | 2.814E+06 | -6.393E+07 | -6.424E+07 |
| Entropy J/kg-K | -2867.262 | -3166.107 | -3166.238 | -3210.364 | -3332.016 | -3230.385 | -8780.748 | -9030.871 |
| Density kg/cum | 801.122 | 761.033 | 763.808 | 770.302 | 768.931 | 854.044 | 974.200 | 993.515 |
| Average MW | 78.116 | 92.343 | 92.343 | 92.137 | 98.140 | 80.846 | 18.015 | 18.015 |
| Liq Vol 60F cum/sec | 3.659E-03 | 1.093E-03 | 1.093E-03 | 1.054E-03 | 3.964E-05 | 6.089E-03 | 4.059E-03 | 4.059E-03 |

(*continued on next page*)

| Stream | 39 | 40 | 41 | 42 | 46 | BENZENE | BOT204 | CW0 |
|---|---|---|---|---|---|---|---|---|
| To | | E216 | | E217 | P208 | | P207 | |
| From | E216 | | E217 | | M5 | E215 | C204 | E203 |
| State | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID |
| Mass Flow tonne/day | | | | | | | | |
| n-Pentane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| n-Hexane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Iso-Pentane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 2-Methyl pentane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Cis-2-Hexene | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Methylcyclopentane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.000 | 0.000 |
| Benzene | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 278.939 | 0.241 | 0.000 |
| Toluene | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.060 | 7.789 | 0.000 |
| *o*-Xylene | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 1.825 | 0.000 |
| Sulfolane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 1554.846 | 0.000 |
| water | 140.000 | 140.000 | 6.000 | 6.000 | 20.701 | 0.000 | 3.156 | 900.000 |
| Total Flow kmol/sec | 0.0899 | 0.0899 | 0.0039 | 0.0039 | 0.0133 | 0.0413 | 0.1530 | 0.5782 |
| Total Flow tonne/day | 140.000 | 140.000 | 6.000 | 6.000 | 20.701 | 279.000 | 1567.858 | 900.000 |
| Total Flow cum/sec | 1.664E-03 | 1.631E-03 | 7.147E-05 | 6.990E-05 | 2.447E-04 | 3.753E-03 | 1.666E-02 | 1.068E-02 |
| Temperature C | 45.029 | 25.000 | 47.386 | 25.000 | 39.960 | 38.300 | 212.720 | 43.462 |
| Pressure kg/sqcm | 1.033 | 1.033 | 1.033 | 1.033 | 1.033 | 1.508 | 0.617 | 1.033 |
| Vapor Frac | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Liquid Frac | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Enthalpy J/kg | -1.578E+07 | -1.586E+07 | -1.577E+07 | -1.586E+07 | -1.580E+07 | 6.529E+05 | -3.365E+06 | -1.579E+07 |
| Enthalpy Watt | -2.557E+07 | -2.570E+07 | -1.095E+06 | -1.101E+06 | -3.786E+06 | 2.108E+06 | -6.107E+07 | -1.644E+08 |
| Entropy J/kg-K | -8778.097 | -9030.871 | -8748.783 | -9030.871 | -8841.437 | -3154.119 | -3905.579 | -8797.631 |
| Density kg/cum | 973.990 | 993.515 | 971.663 | 993.515 | 978.972 | 860.385 | 1089.339 | 975.533 |
| Average MW | 18.015 | 18.015 | 18.015 | 18.015 | 18.015 | 78.116 | 118.611 | 18.015 |
| Liq Vol 60F cum/sec | 1.624E-03 | 1.624E-03 | 6.958E-05 | 6.958E-05 | 2.401E-04 | 3.659E-03 | 1.443E-02 | 1.044E-02 |

(*continued on next page*)

| Stream | CW1 | CWI | CWIN | CWN | CWO | CWOUT | CWT | EXTRACT |
|---|---|---|---|---|---|---|---|---|
| To | E203 | E212 | E205 | E201 | | | | V204 |
| From | | | | | E212 | E205 | E201 | P210 |
| State | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID |
| Mass Flow tonne/day | | | | | | | | |
| n-Pentane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| n-Hexane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.006 |
| Iso-Pentane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 2-Methyl pentane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Cis-2-Hexene | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.699 |
| Methylcyclopentane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 2.732 |
| Benzene | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 296.410 |
| Toluene | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 80.833 |
| *o*-Xylene | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 1.393 |
| Sulfolane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| water | 900.000 | 1000.000 | 3000.000 | 300.000 | 1000.000 | 3000.000 | 300.000 | 0.003 |
| Total Flow kmol/sec | 0.5782 | 0.6425 | 1.9274 | 0.1927 | 0.6425 | 1.9274 | 0.1927 | 0.0547 |
| Total Flow tonne/day | 900.000 | 1000.000 | 3000.000 | 300.000 | 1000.000 | 3000.000 | 300.000 | 382.075 |
| Total Flow cum/sec | 1.048E-02 | 1.165E-02 | 3.495E-02 | 3.495E-03 | 1.186E-02 | 3.565E-02 | 3.577E-03 | 5.185E-03 |
| Temperature C | 25.000 | 25.000 | 25.000 | 25.000 | 42.798 | 45.057 | 48.253 | 41.140 |
| Pressure kg/sqcm | 1.033 | 1.000 | 1.033 | 1.033 | 1.000 | 1.033 | 1.033 | 14.562 |
| Vapor Frac | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Liquid Frac | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Enthalpy J/kg | -1.586E+07 | -1.586E+07 | -1.586E+07 | -1.586E+07 | -1.579E+07 | -1.578E+07 | -1.577E+07 | 5.292E+05 |
| Enthalpy Watt | -1.652E+08 | -1.835E+08 | -5.506E+08 | -5.506E+07 | -1.827E+08 | -5.479E+08 | -5.475E+07 | 2.340E+06 |
| Entropy J/kg-K | -9030.871 | -9030.869 | -9030.871 | -9030.871 | -8805.920 | -8777.745 | -8738.022 | -3225.807 |
| Density kg/cum | 993.515 | 993.515 | 993.515 | 993.515 | 976.186 | 973.962 | 970.805 | 852.901 |
| Average MW | 18.015 | 18.015 | 18.015 | 18.015 | 18.015 | 18.015 | 18.015 | 80.846 |
| Liq Vol 60F cum/sec | 1.044E-02 | 1.160E-02 | 3.479E-02 | 3.479E-03 | 1.160E-02 | 3.479E-02 | 3.479E-03 | 5.035E-03 |

(*continued on next page*)

| Stream | F | FEED | NONARMTS | O+N | TOLUENE | UP204 | UP204A | XYLENE |
|---|---|---|---|---|---|---|---|---|
| To | C201 | V201 | | | | E205 | V203 | |
| From | P201 | | M2 | V204 | E216 | C204 | E205 | E217 |
| State | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | VAPOR | LIQUID | LIQUID |
| Mass Flow tonne/day | | | | | | | | |
| n-Pentane | 29.720 | 29.720 | 29.720 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| n-Hexane | 54.940 | 54.940 | 54.934 | 0.006 | 0.000 | 0.007 | 0.007 | 0.000 |
| Iso-Pentane | 25.840 | 25.840 | 25.840 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 2-Methyl pentane | 130.180 | 130.180 | 130.180 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Cis-2-Hexene | 6.790 | 6.790 | 6.089 | 0.698 | 0.000 | 0.845 | 0.845 | 0.000 |
| Methylcyclopentane | 13.450 | 13.450 | 10.718 | 2.731 | 0.000 | 3.304 | 3.304 | 0.000 |
| Benzene | 299.970 | 299.970 | 3.555 | 17.410 | 0.020 | 358.458 | 358.458 | 0.000 |
| Toluene | 85.820 | 85.820 | 4.985 | 0.000 | 79.162 | 97.754 | 97.754 | 1.612 |
| *o*-Xylene | 3.290 | 3.290 | 1.897 | 0.000 | 0.005 | 1.685 | 1.685 | 1.388 |
| Sulfolane | 0.000 | 0.000 | 0.013 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| water | 0.000 | 0.000 | 0.065 | 0.003 | 0.000 | 20.635 | 20.635 | 0.000 |
| Total Flow kmol/sec | 0.0921 | 0.0921 | 0.0375 | 0.0031 | 0.0099 | 0.0794 | 0.0794 | 0.0004 |
| Total Flow tonne/day | 650.000 | 650.000 | 267.997 | 20.848 | 79.187 | 482.687 | 482.687 | 3.000 |
| Total Flow cum/sec | 9.979E-03 | 9.975E-03 | 4.811E-03 | 2.910E-04 | 1.085E-03 | 3.995E+00 | 6.591E-03 | 4.050E-05 |
| Temperature C | 40.335 | 40.000 | 40.188 | 41.140 | 44.700 | 66.860 | 58.939 | 40.000 |
| Pressure kg/sqcm | 7.138 | 1.033 | 5.000 | 14.562 | 1.233 | 0.564 | 0.564 | 1.289 |
| Vapor Frac | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 1.000 | 0.000 | 0.000 |
| Liquid Frac | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 0.000 | 1.000 | 1.000 |
| Enthalpy J/kg | -5.879E+05 | -5.891E+05 | -2.179E+06 | 3.026E+05 | 1.634E+05 | 3.633E+05 | -1.244E+05 | -1.181E+04 |
| Enthalpy Watt | -4.423E+06 | -4.432E+06 | -6.759E+06 | 7.302E+04 | 1.498E+05 | 2.030E+06 | -6.947E+05 | -4.099E+02 |
| Entropy J/kg-K | -4782.719 | -4783.777 | -7127.970 | -3659.782 | -3600.943 | -1853.407 | -3310.393 | -3821.611 |
| Density kg/cum | 753.866 | 754.202 | 644.708 | 829.295 | 844.444 | 1.399 | 847.624 | 857.308 |
| Average MW | 81.645 | 81.645 | 82.739 | 79.014 | 92.137 | 70.357 | 70.357 | 98.140 |
| Liq Vol 60F cum/sec | 9.723E-03 | 9.723E-03 | 4.689E-03 | 2.822E-04 | 1.054E-03 | 6.328E-03 | 6.328E-03 | 3.964E-05 |

## 4.7 Performance Index

Performance of complete aromatic recovery unit with liquid-liquid extraction can be can be evaluated by Performance Index (*PI*). *PI* can be defined as the product of solvent selectivity, $S_s$ and solvent capacity, $S_c$.

$$PI = S_s \times S_c \tag{4.5}$$

$$S_s = \left( \frac{x_a^e / x_a^r}{x_n^e / x_n^r} \right) \tag{4.6}$$

$$S_c = \left( x_a^e / x_a^r \right). \tag{4.7}$$

Where,

$x_a^e$: is the mole fraction of aromatics in the extract phase, stream EXTRACT.

$x_a^r$ : is the mole fraction of aromatics in the raffinate phase, stream NONARMTS.

$x_n^e$: is the mole fraction of non-aromatics in the extract phase, stream EXTRACT.

$x_n^e$: is the mole fraction of non-aromatics in the raffinate phase, stream NONARMTS.

Performance index calculation for complete aromatic recovery unit with pure sulfolane as solvent is given in Table 4.23.

Table 4.23 Performance index of pure sulfolane for extraction aromatic recovery unit

| $x_a^e$ | $x_a^r$ | $x_n^e$ | $x_n^r$ | $S_c$ | $S_s$ | *PI* |
|---|---|---|---|---|---|---|
| 0.9913 | 0.0363 | 0.0086 | 0.9626 | 27.3309 | 3044.8713 | **83218.9269** |

## 4.8 Conclusions

Aromatic recovery unit with liquid-liquid extraction has been simulated with ASPEN PLUS 10.2 a sequential modular simulation package. RK-SOAVE property method is used for vapor-liquid calculations in all distillation columns and UNIF-LL property method is used for liquid-liquid calculations in all extraction columns. For the simulation to reflect real world, validation with plant data was taken up. This simulation can be used for troubleshooting, de-bottlenecking and revamping studies after modifying it for the corresponding throughputs.

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# Chapter 5

# SIMULATION OF AROMATIC RECOVERY FLOWSHEET USING MIXED SOLVENTS

## 5.1 Introduction

A variety of solvents for the extraction of aromatics have been described and tested by various investigators. A comprehensive list of these solvents is given in Table 5.1.

Table 5.1 Reported solvents for aromatic extraction

| Sl. No. | Solvent | Reference |
|---|---|---|
| 1 | Sulfolane | [1-9] |
| 2 | 3-methyl sulfolane | [10] |
| 3 | 2-mercaptoethanol | [10] |
| 4 | Dimethyl sulfoxide | [1] |
| 5 | N-methyl-2-pyrrolidone | [1, 2, 7, 8, 11, 12, 17] |
| 6 | Ethylene carbonate | [2, 13] |
| 7 | Propylene carbonate | [2, 14] |
| 8 | N-methyl formamide | [15] |
| 9 | N,N-dimethyl formamide | [1, 2, 7, 13, 16, 17] |
| 10 | Furfural | [1, 2] |
| 11 | Morpholine | [15] |
| 12 | N-formyl morpholine | [18] |
| 13 | Phenol | [1, 2, 19] |
| 14 | Furfuryl alcohol | [20] |
| 15 | Benzyl alcohol | [21] |
| 16 | Isophorone | [15] |
| 17 | Thiodiglycol | [10] |
| 18 | Ethylene glycol | [2, 12, 16] |
| 19 | Diethylene glycol | [1, 2, 5, 9, 21] |
| 20 | Triethylene glycol | [1, 2, 7, 8, 14] |
| 21 | Tetraethylene glycol | [5, 22] |
| 22 | Dipropylene glycol | [5] |
| 23 | Hexylene glycol | [15] |
| 24 | Diethanol amine | [5] |
| 25 | Triethylene glycol dimethyl ether | [15] |
| 26 | Triethylene glycol ethyl ether | [15] |
| 27 | Triethylene glycol butyl ether | [15] |
| 28 | Tetraethylene glycol dimethyl ether | [15] |
| 29 | Diethylene glycol dimethyl ether | [15] |
| 30 | Diethylene glycol propyl ether | [15] |
| 31 | Diethylene glycol diethyl ether | [15] |
| 32 | Diethylene glycol monobutyl ether | [15] |
| 33 | Diethylene glycol di-n-butyl ether | [15] |

N.B.: Water can be used as co solvent

Some investigators have examined the mixed solvents i.e., the mixture of any two of those solvents [2, 13, 16] which are also used for effective separation of aromatics.

## 5.2 Simulation using mixed solvents

The simulation programme developed for sulfolane (TMS) as described in chapter 4 has been used to get the performance of mixed solvents. The solvent input stream, 5C to extraction column, C201 was detached to introduce co solvent into the flowsheet with all the other input specifications remains unchanged. We started with pure sulfolane (100 % TMS) and gradually increasing the amount (1mass %) of the other solvents and reducing the amount of TMS (i.e., 99 mass % TMS +1 mass % other solvent then in the next step 98 mass % TMS + 2 mass % other solvent). Simulations have been done until any serious error encountered in the convergence of flowsheet, it means flowsheet required major modifications. Out of 33 solvent listed in Table 5.1 we have chosen N-methyl-2-pyrrolidone (NMP), Triethylene glycol (TEG), Tetraethylene glycol (TeEG), Dimethyl sulfoxide (DMSO), and N-methyl formamide (NMF) as co solvent with sulfolane (TMS) to test the performance of mixed solvents. Performance index (*PI*) as defined in chapter 4 can be used to compare the mixed solvent performance. Relative performance index (*RPI*) can be defined as,

$$RPI = \left( \frac{PI_{MIXED}}{PI_{TMS}} \right) \tag{5.1}$$

Since we detached the solvent input stream, 5C to extraction column, C201 we may likely to loose solvents in extract stream, EXTRACT and non aromatic product stream, NONARMTS. So, we also compared performance of mixed solvents in terms of performance index without solvent loss ($PI^l$),

$$PI^l = \left[ \frac{PI}{S_{in}} \right] \tag{5.2}$$

$$S^l = \left[ S_{in} - \left( E \times x_s^e + N \times x_s^n \right) \right] \tag{5.3}$$

Relative performance index with solvent loss ($RPI^l$) can be defined as,

$$RPI^l = \left( \frac{PI^l_{MIXED}}{PI^l_{TMS}} \right) \tag{5.3}$$

Where,

$S_{in}$ : Amount of solvent entering the extraction column, C201 i.e., mole flow rate of stream 5C.

$E$ : Molar flow rate of extract phase, stream EXTRACT.

$x_s^e$ : Mole fraction of solvent in extract phase, stream EXTRACT.

$N$ : Molar flow rate of non-aromatic product, stream NONARMTS.

$x_s^n$ : Mole fraction of solvent in non-aromatic product, stream NONARMTS.

$PI_{TMS}$ : Performance index of pure sulfolane without solvent loss.

$PI_{MIXED}$ : Performance index of mixed solvent without solvent loss.

$PI'_{TMS}$ : Performance index of pure sulfolane with solvent loss.

$PI'_{MIXED}$ : Performance index of mixed solvent with solvent loss.

## 5.3 Results and discussion

Performance index of mixed solvents both with and without solvent loss are given in Table 5.2. Relative performance index without and with solvent loss against solvent increment in TMS are respectively shown in Figure 5.1 and 5.2.

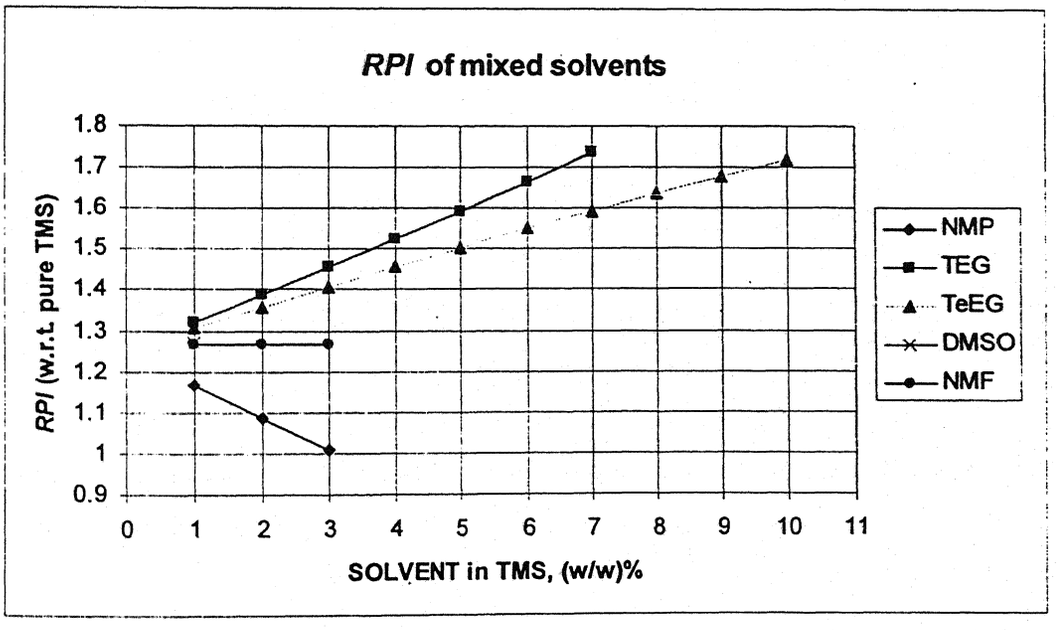


Figure 5.1 Relative performance indexes without solvent loss.

Table 5.2 Performance index of mixed solvents for extraction aromatic recovery unit

| Mixed solvent, mass % | | $x_a^e$ | $x_a^r$ | $x_n^e$ | $x_n^r$ | $S^I$ | $S_c$ | $S_s$ | $PI$ | $RPI$ | $PI^I$ | $RPI^I$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TMS | NMP | | | | | | | | | | | |
| 100 | 0 | 0.9913 | 0.0363 | 0.0086 | 0.9626 | 1.1960E-03 | 27.3309 | 3044.8713 | 83218.9269 | 1.0000 | 6.9582E+07 | 1.0000 |
| 99 | 1 | 0.9935 | 0.0396 | 0.0062 | 0.9590 | 1.6317E-03 | 25.0844 | 3863.9085 | 96923.8129 | 1.1647 | 5.9399E+07 | 0.8537 |
| 98 | 2 | 0.9925 | 0.0399 | 0.0066 | 0.9587 | 2.3661E-03 | 24.8982 | 3622.4264 | 90191.8457 | 1.0838 | 3.8118E+07 | 0.5478 |
| 97 | 3 | 0.9915 | 0.0402 | 0.0070 | 0.9582 | 3.1116E-03 | 24.6815 | 3396.5534 | 83832.1014 | 1.0074 | 2.6942E+07 | 0.3872 |
| TMS | TEG | | | | | | | | | | | |
| 99 | 1 | 0.9943 | 0.0390 | 0.0057 | 0.9597 | 1.2681E-03 | 25.4777 | 4311.4413 | 109845.6852 | 1.3200 | 8.6622E+07 | 1.2449 |
| 98 | 2 | 0.9945 | 0.0388 | 0.0055 | 0.9600 | 1.2665E-03 | 25.6557 | 4498.6594 | 115416.0929 | 1.3869 | 9.1128E+07 | 1.3096 |
| 97 | 3 | 0.9947 | 0.0385 | 0.0053 | 0.9602 | 1.2651E-03 | 25.8177 | 4692.0505 | 121137.8942 | 1.4557 | 9.5757E+07 | 1.3762 |
| 96 | 4 | 0.9949 | 0.0383 | 0.0051 | 0.9605 | 1.2637E-03 | 25.9686 | 4883.4861 | 126817.4448 | 1.5239 | 1.0036E+08 | 1.4423 |
| 95 | 5 | 0.9950 | 0.0381 | 0.0049 | 0.9607 | 1.2624E-03 | 26.1057 | 5078.1030 | 132567.5897 | 1.5930 | 1.0501E+08 | 1.5092 |
| 94 | 6 | 0.9952 | 0.0379 | 0.0048 | 0.9608 | 1.2611E-03 | 26.2379 | 5275.9688 | 138430.3243 | 1.6634 | 1.0977E+08 | 1.5776 |
| 93 | 7 | 0.9953 | 0.0377 | 0.0046 | 0.9610 | 1.2599E-03 | 26.3789 | 5479.8616 | 144552.7605 | 1.7370 | 1.1474E+08 | 1.6490 |
| TMS | TeEG | | | | | | | | | | | |
| 99 | 1 | 0.9943 | 0.0391 | 0.0057 | 0.9597 | 1.2687E-03 | 25.4382 | 4272.6073 | 108687.4760 | 1.3060 | 8.5668E+07 | 1.2312 |
| 98 | 2 | 0.9944 | 0.0389 | 0.0056 | 0.9599 | 1.2678E-03 | 25.5698 | 4415.3611 | 112900.0759 | 1.3567 | 8.9055E+07 | 1.2799 |
| 97 | 3 | 0.9946 | 0.0387 | 0.0054 | 0.9600 | 1.2669E-03 | 25.6809 | 4553.5749 | 116939.9882 | 1.4052 | 9.2302E+07 | 1.3265 |
| 96 | 4 | 0.9947 | 0.0386 | 0.0053 | 0.9602 | 1.2661E-03 | 25.7884 | 4694.5567 | 121065.0451 | 1.4548 | 9.5619E+07 | 1.3742 |
| 95 | 5 | 0.9948 | 0.0384 | 0.0052 | 0.9603 | 1.2653E-03 | 25.8929 | 4825.4872 | 124946.0712 | 1.5014 | 9.8745E+07 | 1.4191 |
| 94 | 6 | 0.9949 | 0.0383 | 0.0050 | 0.9605 | 1.2645E-03 | 25.9952 | 4959.2627 | 128916.8208 | 1.5491 | 1.0195E+08 | 1.4652 |
| 93 | 7 | 0.9950 | 0.0382 | 0.0049 | 0.9606 | 1.2639E-03 | 26.0771 | 5086.0041 | 132628.1126 | 1.5937 | 1.0494E+08 | 1.5081 |
| 92 | 8 | 0.9951 | 0.0381 | 0.0048 | 0.9607 | 1.2634E-03 | 26.1376 | 5212.0942 | 136231.4359 | 1.6370 | 1.0783E+08 | 1.5497 |
| 91 | 9 | 0.9952 | 0.0380 | 0.0047 | 0.9608 | 1.2628E-03 | 26.2016 | 5329.4126 | 139639.0549 | 1.6780 | 1.1058E+08 | 1.5892 |
| 90 | 10 | 0.9953 | 0.0379 | 0.0046 | 0.9609 | 1.2623E-03 | 26.2617 | 5441.4599 | 142901.7796 | 1.7172 | 1.1321E+08 | 1.6270 |
| TMS | DMSO | | | | | | | | | | | |
| 99 | 1 | 0.9926 | 0.0389 | 0.0059 | 0.9599 | 2.7153E-03 | 25.5031 | 4147.9457 | 105785.3628 | 1.2712 | 3.8959E+07 | 0.5599 |
| TMS | NMF | | | | | | | | | | | |
| 99 | 1 | 0.9933 | 0.0390 | 0.0059 | 0.9598 | 1.9872E-03 | 25.4564 | 4133.5552 | 105225.5913 | 1.2644 | 5.2952E+07 | 0.7610 |
| 98 | 2 | 0.9921 | 0.0389 | 0.0059 | 0.9599 | 3.1591E-03 | 25.4992 | 4129.8454 | 105307.8895 | 1.2654 | 3.3334E+07 | 0.4791 |
| 97 | 3 | 0.9909 | 0.0388 | 0.0059 | 0.9600 | 4.3316E-03 | 25.5352 | 4120.3155 | 105213.2791 | 1.2643 | 2.4290E+07 | 0.3491 |

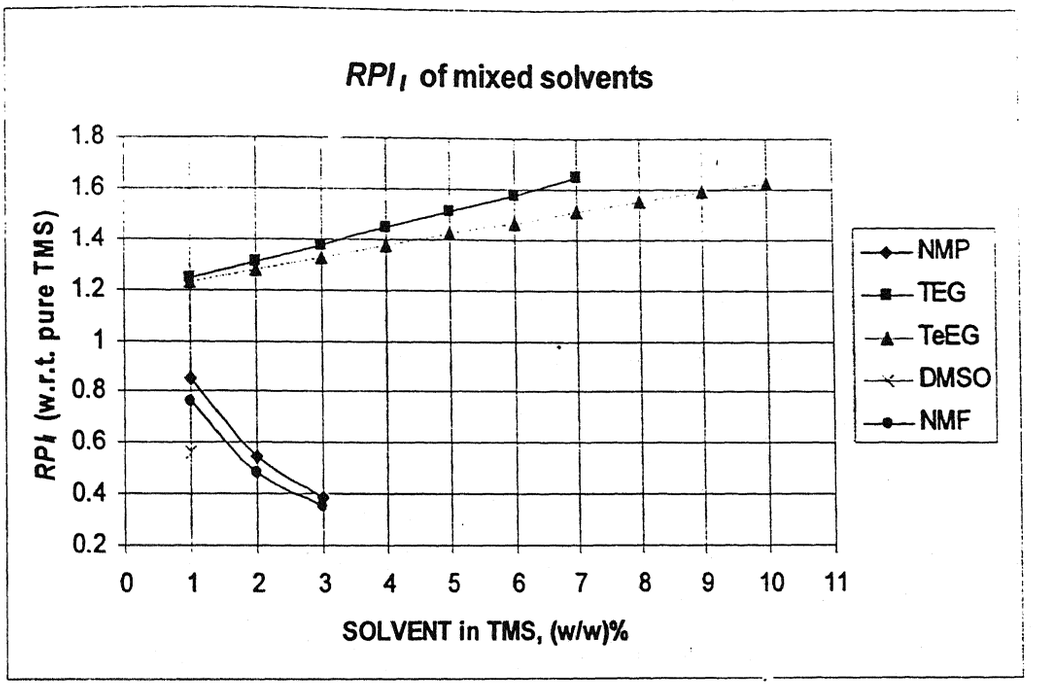


Figure 5.2 Relative performance indexes with solvent loss.

Both relative performance index, without and with solvent loss for TEG and TeEG is increasing with increasing mass percent of these solvent in TMS. Thus we will get more aromatics in the extract stream, EXTRACT. Where as, in the case of mixed solvents with NMP we are getting decreasing performances with increasing TMS in NMP. This is because of the low boiling point of NMP, 477.42 °K as compared to 560.45 °K of sulfolane.

## 5.5 Conclusions

N-methyl-2-pyrrolidone, Triethylene glycol, Tetraethylene glycol, Dimethyl sulfoxide, and N-methyl formamide have been chosen as co solvent with sulfolane to study the performance of mixed solvents. It is found that triethylene glycol and tetraethylene glycol as a co solvent gives better performance than other three co solvents.

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# Chapter 6

# SIMULATION OF AROMATIC RECOVERY FLOWSHEET USING EXTRACTIVE DISTILLATION

## 6.1 Introduction

Extractive distillation (ED) is a vapor-liquid process operation that uses a third component, or solvent, to effect a chemical separation. The extractive agent creates or enhances the volatility difference between the components to be separated. The extractive agent and the less volatile component flow to the bottom of the distillation column, where the extracted component is recovered by a subsequent distillation. The non-extracted species are distilled to the top of the extractive distillation tower.

ED has many applications within the refining and petrochemical industries for the recovery of high-purity products. Some of the well-known applications include aromatics such as benzene, toluene and xylene (BTX), butadiene, isoprene, and styrene recovery. ED is a very efficient processing technique because of its low capital and operating costs, and operational ease and flexibility. Its application is notable in BTX recovery [1, 2], where it has become the preferred method for producing high-purity products.

The key feature of an ED process is the solvent, which enhances the relative volatility of certain feed components or breaks azeotropes among components, leading to their separation as the desired product in a distillation operation. The purpose of this work was to simulate extractive distillation process, using sulfolane for the same naphtha and solvent feed as used for BTX recovery by liquid-liquid extraction (LLE) process in chapter 4.

Figure 6.1 shows the simplified diagram of extractive distillation process. The extractive distillation process separates aromatics from naphtha. It minimizes aromatic content in gasoline and refines extracted aromatics to be used as raw materials of petrochemical products. Many solvents such as sulfolane, N-Methyl Pyrrolidone [1], N-Formyl Morpholine [3], and certain Glycol blends [1] are used to extract BTX by extractive distillation. For our case sulfolane is used as solvent. Injection of solvent that have good affinity with aromatics and less affinity with non-aromatics reduces the relative volatility of aromatics.

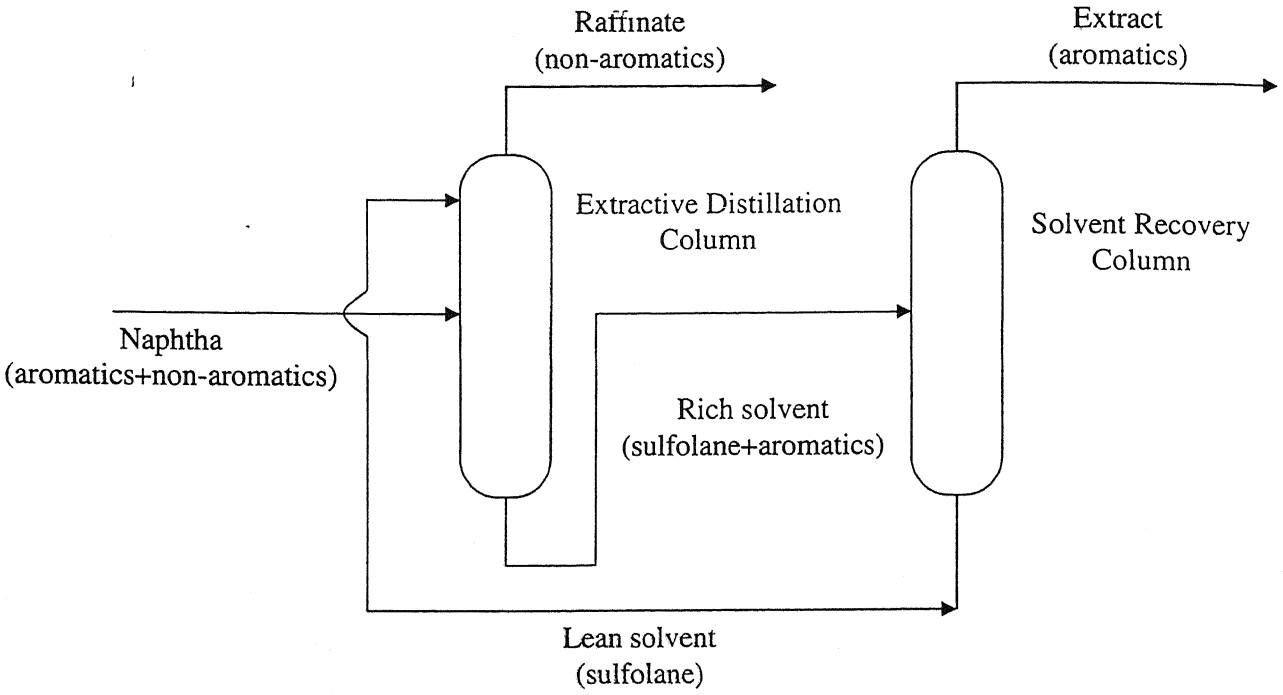



Figure 6.1 Simplified diagram of extractive distillation process

This causes the collection of aromatics and solvent at the bottom of extractive distillation column. Aromatics gather at the top and sulfolane at the bottom in subsequent stripper column, which is connected with the bottom of the extractive distillation column. Then sulfolane is recycled to the extractive distillation column.

## 6.2 Simulation of Extractive Distillation Column

### 6.2.1 Initial input specifications

Simulation of the extractive distillation column is performed by using the rigorous distillation model RADFRAC from ASPEN PLUS simulator [4]. Figure 6.2 shows the column configuration for simulation of extractive distillation, and Table 6.1 and Table 6.2 shows initial simulation input data. Shortcut design model DSTWU from ASPEN PLUS simulator has been used to calculate initial input specification for number of stages, distillate rate and reboiler duty. Other specifications such as streams, pressure, reboiler, flash, and splitter specifications are taken from literature [3].

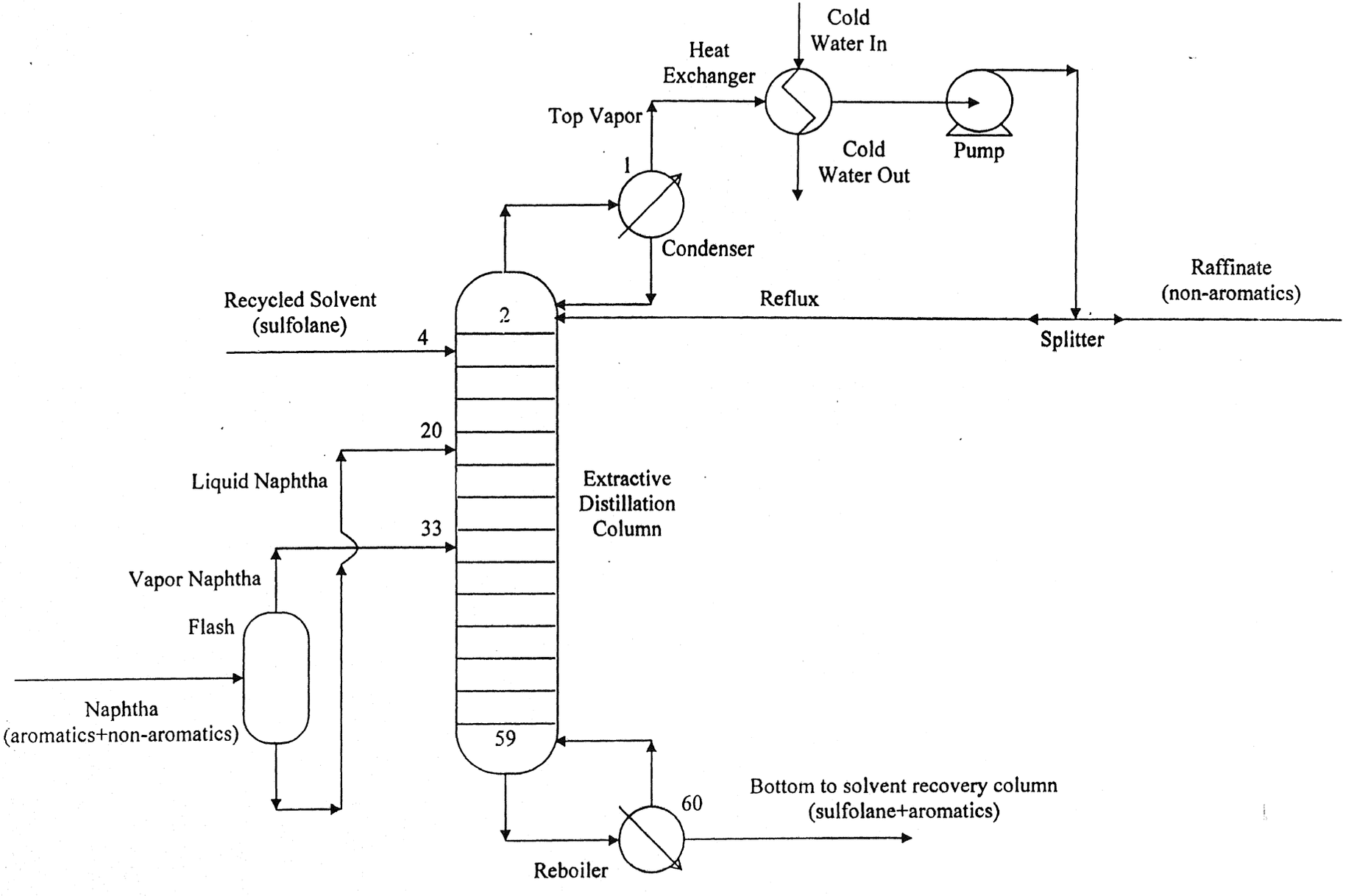



Figure 6.2 Configuration of Extractive Distillation Column

Table 6.1 Initial specifications for extractive distillation column [3]

| Column Specifications | | Column Specifications | |
|---|---|---|---|
| **Configuration** | | **Block options** | |
| Number of stages | 60 | Property method | RK-SOAVE |
| Condenser | Partial vapor | **Properties** | |
| Reboiler | Thermosyphon | 1 to 60 | RK-SOAVE |
| Valid phases | Vapor-liquid-liquid | 4 to 19 | NRTL-2 |
| Convergence | Standard | **Pressure**, kg/sqcm | |
| Distillate rate, MT/D | 1600 | Top pressure | 1.4 |
| Reboiler duty, MMkcal/hr | 20 | Pressure drop | 0.5 |
| **Streams** | | **Reboiler** | |
| Reflux | 2 | Outlet temperature, C | 162 |
| Solvent Feed | 4 | Reboiler pressure, kg/sqcm | 1.9 |
| Liquid Naphtha Feed | 20 | **3-phase** | |
| Vapor-Naphtha-Feed | 33 | Stages | 2 to 59 |
| Top Vapor Product | 1 | Key components, 2nd liquid phase | Non-aromatics and water |
| Bottom Product | 60 | **Convergence** | |
| **Column type** | | Algorithm | Standard |
| 2 to 59 | Sieve Trays | Tears | Broyden |

Table 6.2 Initial specifications of other blocks for extractive distillation [3]

| Block | Specifications | Value |
|---|---|---|
| Flash | Pressure | 2 kg/sqcm |
| | Vapor fraction | 0.2 |
| Heat Exchanger | Hot stream outlet vapor fraction | 0 |
| Pump | Discharge pressure | 2 kg/sqcm |
| Splitter | Split fraction, Reflux | 0.82816 |

### 6.2.2 Property method

Since extractive distillation require vapor-liquid-liquid calculations, it is necessary to use a property method which is equally applicable to both vapor-liquid and liquid-liquid calculations or different property method for vapor-liquid and liquid-liquid calculations. For our case NRTL-2 is used for liquid-liquid and RK-SOAVE is used for vapor-liquid calculations. Property method selection form is shown in Figure 6.3. The valid phases from introduction stage of lean solvent, 4, to one stage above the liquid naphtha feed stage, 19, are vapor-liquid-liquid phases. Thus, for stage 1-60 RK-SOAVE and for stage 4-19 NRTL-2 is used. RK-SOAVE is used as base/global property method.

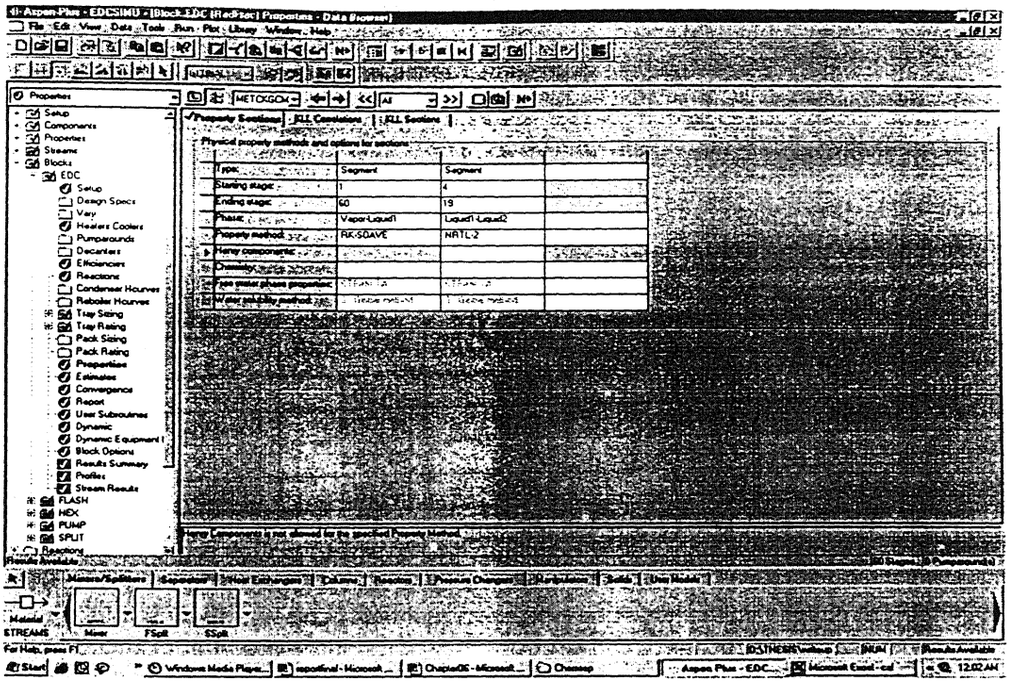


Figure 6.3 Property method selection form for extractive distillation column.

### 6.2.3 Efficiencies

ChemSep software is used to get murphree efficiencies for extractive distillation column. Input specifications for ChemSep simulation is given in Table 6.3.

Table 6.3 ChemSep input specifications for extractive distillation column.

| Specifications | | | |
|---|---|---|---|
| Operation | NonEquilibrium Column | Hole diameter, m | 0.005-0.012 |
| Type | Extractive Distillation | Hole pitch, m | 0.032 |
| Column internals | Sieve tray | Active area, % total | **60.000** |
| Column diameter, m | **5.300** | Total hole area, % active | 12.000 |
| Tray spacing, m | 0.800 | Downcomer area, % total | 12.000 |
| Number of flow passes | 1 | Weir type | Segmental |
| Liquid flow path length, m | 1.600 | Weir length, m | **4.018** |
| Downcomer clearance, m | 0.0381 | Weir height, m | 0.0508 |
| Deck thickness, m | 0.003404 | | |

Column diameter, active area and weir length are calculated from tray sizing calculations in ASPEN PLUS. Tray sizing result is given in Table 6.4. Specifications corresponding to tray with maximum diameter from ASPEN PLUS tray sizing calculations are used as input in ChemSep.

Table 6.4 Tray sizing results for extractive distillation column

| Stage Range | Diameter[a], m | Side downcomer velocity[b], m/s | Side weir length[b], m | Total area[b], sqm | Active area[b], sqm | Side downcomer area[b], sqm |
|---|---|---|---|---|---|---|
| 2 – 3 | 4.991 | 0.0395 | 3.814 | 19.561 | 14.867 | 2.347 |
| 4 – 19 | **5.257** | 0.0434 | **4.018** | **21.705** | **16.496** | 2.605 |
| 20 – 32 | 5.119 | 0.0467 | 3.912 | 20.584 | 15.644 | 2.470 |
| 33 – 59 | 4.835 | 0.0479 | 3.695 | 18.363 | 13.956 | 2.204 |
| [a]Diameter of stage with maximum diameter: [b]Corresponding to stage with maximum diameter | | | | | | |

Other specifications such as downcomer clearance, deck thickness, hole diameter, hole pitch and weir height are taken from literature [5]. Murphree efficiencies obtained from ChemSep are reported in Table 6.5. Efficiency plot is shown in Figure 6.4.

Table 6.5 Murphree efficiencies for extractive distillation column

| Stage | N-P | N-H | 2-MB | 2-MP | C-2-HE | MCP | BZ | TOL | OX | TMS |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| 2 | 0.6706 | 0.6644 | 0.6439 | 0.6600 | 0.6762 | 0.8426 | 0.5881 | 0.7425 | 0.7476 | 0.7553 |
| 3 | 0.6613 | 0.6564 | 0.6355 | 0.6556 | 0.6667 | 0.7485 | 1.0000 | 0.7443 | 0.7500 | 0.7578 |
| 4 | 0.6670 | 0.7184 | 0.6401 | 0.6111 | 0.6806 | 0.7817 | 0.7549 | 0.7701 | 0.7748 | 0.9930 |
| 5 | 0.6524 | 0.7017 | 0.6200 | 0.5447 | 0.6663 | 0.6922 | 0.7596 | 0.7846 | 0.7920 | 0.6959 |
| 6 | 0.6485 | 0.7074 | 0.6160 | 0.0001 | 0.6621 | 0.6941 | 0.7616 | 0.7861 | 0.7936 | 0.6651 |
| 7 | 0.6469 | 0.7127 | 0.6150 | 0.8198 | 0.6603 | 0.7039 | 0.7626 | 0.7864 | 0.7939 | 0.6639 |
| 8 | 0.6463 | 0.7159 | 0.6154 | 0.7561 | 0.6595 | 0.7116 | 0.7629 | 0.7864 | 0.7940 | 0.6652 |
| 9 | 0.6466 | 0.7174 | 0.6172 | 0.7375 | 0.6596 | 0.7163 | 0.7630 | 0.7864 | 0.7940 | 0.6633 |
| 10 | 0.6480 | 0.7176 | 0.6216 | 0.7297 | 0.6607 | 0.7185 | 0.7628 | 0.7863 | 0.7940 | 0.6562 |
| 11 | 0.6513 | 0.7170 | 0.6303 | 0.7260 | 0.6633 | 0.7188 | 0.7625 | 0.7860 | 0.7938 | 0.6416 |
| 12 | 0.6576 | 0.7156 | 0.6458 | 0.7242 | 0.6683 | 0.7176 | 0.7620 | 0.7858 | 0.7936 | 0.6158 |
| 13 | 0.6681 | 0.7133 | 0.6687 | 0.7232 | 0.6768 | 0.7150 | 0.7614 | 0.7854 | 0.7933 | 0.5704 |
| 14 | 0.6835 | 0.7098 | 0.6955 | 0.7229 | 0.6899 | 0.7105 | 0.7606 | 0.7849 | 0.7929 | 0.4831 |
| 15 | 0.7028 | 0.7042 | 0.7201 | 0.7229 | 0.7079 | 0.7031 | 0.7596 | 0.7842 | 0.7924 | 0.2804 |
| 16 | 0.7229 | 0.6946 | 0.7390 | 0.7231 | 0.7298 | 0.6899 | 0.7581 | 0.7833 | 0.7916 | 0.0001 |
| 17 | 0.7407 | 0.6748 | 0.7525 | 0.7234 | 0.7531 | 0.6623 | 0.7562 | 0.7820 | 0.7905 | 1.0000 |
| | | | | | | | | | | |

*(continued on next page)*

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 18 | 0.7552 | 0.6132 | 0.7633 | 0.7237 | 0.7751 | 0.5757 | 0.7533 | 0.7801 | 0.7890 | 1.0000 |
| 19 | 0.9515 | 0.6948 | 0.9769 | 0.7028 | 0.9631 | 0.3652 | 0.7200 | 0.7498 | 0.7596 | 1.0000 |
| 20 | 0.6533 | 0.7130 | 0.6192 | 0.7516 | 0.6664 | 0.7025 | 0.7012 | 0.6841 | 0.6753 | 0.6604 |
| 21 | 0.6524 | 0.7165 | 0.6188 | 0.7362 | 0.6651 | 0.7093 | 0.7099 | 0.6917 | 0.6824 | 0.6635 |
| 22 | 0.6518 | 0.7179 | 0.6187 | 0.7286 | 0.6639 | 0.7133 | 0.7162 | 0.6970 | 0.6874 | 0.6652 |
| 23 | 0.6520 | 0.7182 | 0.6199 | 0.7244 | 0.6632 | 0.7152 | 0.7209 | 0.7000 | 0.6903 | 0.6650 |
| 24 | 0.6534 | 0.7177 | 0.6232 | 0.7216 | 0.6630 | 0.7157 | 0.7248 | 0.7016 | 0.6913 | 0.6628 |
| 25 | 0.6562 | 0.7167 | 0.6299 | 0.7196 | 0.6633 | 0.7151 | 0.7286 | 0.7026 | 0.6910 | 0.6583 |
| 26 | 0.6612 | 0.7152 | 0.6414 | 0.7179 | 0.6644 | 0.7137 | 0.7328 | 0.7045 | 0.6902 | 0.6509 |
| 27 | 0.6685 | 0.7131 | 0.6578 | 0.7165 | 0.6667 | 0.7113 | 0.7373 | 0.7099 | 0.6904 | 0.6390 |
| 28 | 0.6783 | 0.7102 | 0.6770 | 0.7153 | 0.6706 | 0.7075 | 0.7420 | 0.7220 | 0.6959 | 0.6194 |
| 29 | 0.6899 | 0.7059 | 0.6950 | 0.7142 | 0.6766 | 0.7009 | 0.7463 | 0.7413 | 0.7164 | 0.5846 |
| 30 | 0.7018 | 0.6989 | 0.7084 | 0.7133 | 0.6852 | 0.6885 | 0.7498 | 0.7615 | 0.7523 | 0.5047 |
| 31 | 0.7117 | 0.6849 | 0.7141 | 0.7124 | 0.6963 | 0.6589 | 0.7520 | 0.7754 | 0.7808 | 0.0001 |
| 32 | 0.9957 | 0.8939 | 0.9980 | 0.7339 | 0.9922 | 0.9009 | 0.0001 | 0.0001 | 0.0001 | 0.9985 |
| 33 | 0.6409 | 0.7013 | 0.6070 | 0.7140 | 0.6563 | 0.6965 | 0.6909 | 0.6776 | 0.6693 | 0.6495 |
| 34 | 0.6396 | 0.7035 | 0.6058 | 0.7109 | 0.6550 | 0.7012 | 0.6951 | 0.6817 | 0.6732 | 0.6511 |
| 35 | 0.6386 | 0.7046 | 0.6048 | 0.7088 | 0.6541 | 0.7045 | 0.6977 | 0.6844 | 0.6760 | 0.6522 |
| 36 | 0.6378 | 0.7049 | 0.6040 | 0.7074 | 0.6533 | 0.7071 | 0.6991 | 0.6859 | 0.6775 | 0.6524 |
| 37 | 0.6371 | 0.7048 | 0.6033 | 0.7062 | 0.6526 | 0.7094 | 0.6998 | 0.6865 | 0.6781 | 0.6519 |
| 38 | 0.6365 | 0.7043 | 0.6027 | 0.7053 | 0.6520 | 0.7118 | 0.7002 | 0.6865 | 0.6780 | 0.6508 |
| 39 | 0.6360 | 0.7037 | 0.6021 | 0.7045 | 0.6515 | 0.7144 | 0.7005 | 0.6861 | 0.6776 | 0.6491 |
| 40 | 0.6355 | 0.7029 | 0.6017 | 0.7038 | 0.6511 | 0.7173 | 0.7012 | 0.6855 | 0.6770 | 0.6467 |
| 41 | 0.6351 | 0.7019 | 0.6012 | 0.7032 | 0.6507 | 0.7205 | 0.7024 | 0.6848 | 0.6761 | 0.6433 |
| 42 | 0.6347 | 0.7007 | 0.6008 | 0.7027 | 0.6503 | 0.7238 | 0.7046 | 0.6840 | 0.6749 | 0.6384 |
| 43 | 0.6343 | 0.6990 | 0.6005 | 0.7022 | 0.6500 | 0.7271 | 0.7082 | 0.6830 | 0.6734 | 0.6309 |
| 44 | 0.6340 | 0.6966 | 0.6001 | 0.7018 | 0.6497 | 0.7300 | 0.7132 | 0.6819 | 0.6715 | 0.6192 |
| 45 | 0.6337 | 0.6928 | 0.5998 | 0.7014 | 0.6494 | 0.7326 | 0.7198 | 0.6806 | 0.6689 | 0.5996 |
| 46 | 0.6334 | 0.6862 | 0.5995 | 0.7011 | 0.6491 | 0.7346 | 0.7173 | 0.6793 | 0.6654 | 0.5647 |
| 47 | 0.6331 | 0.6730 | 0.5992 | 0.7008 | 0.6489 | 0.7362 | 0.7349 | 0.6783 | 0.6607 | 0.4945 |
| 48 | 0.6328 | 0.6379 | 0.5989 | 0.7005 | 0.6486 | 0.7372 | 0.7416 | 0.6789 | 0.6549 | 0.3152 |
| 49 | 0.6325 | 0.3765 | 0.5986 | 0.7002 | 0.6483 | 0.7378 | 0.7468 | 0.6830 | 0.6485 | 0.0001 |
| 50 | 0.6321 | 0.8940 | 0.5981 | 0.7000 | 0.6480 | 0.7379 | 0.7507 | 0.6935 | 0.6432 | 1.0000 |
| 51 | 0.6317 | 0.7960 | 0.5976 | 0.6997 | 0.6476 | 0.7376 | 0.7532 | 0.7108 | 0.6427 | 1.0000 |
| 52 | 0.6311 | 0.7725 | 0.5970 | 0.6994 | 0.6471 | 0.7368 | 0.7546 | 0.7317 | 0.6531 | 1.0000 |
| 53 | 0.6303 | 0.7625 | 0.5961 | 0.6991 | 0.6465 | 0.7354 | 0.7553 | 0.7508 | 0.6799 | 1.0000 |
| 54 | 0.6292 | 0.7572 | 0.5949 | 0.6986 | 0.6456 | 0.7332 | 0.7551 | 0.7648 | 0.7188 | 1.0000 |
| 55 | 0.6278 | 0.7538 | 0.5932 | 0.6980 | 0.6444 | 0.7299 | 0.7542 | 0.7737 | 0.7542 | 1.0000 |
| 56 | 0.6257 | 0.7511 | 0.5908 | 0.6970 | 0.6426 | 0.7246 | 0.7522 | 0.7785 | 0.7762 | 0.0001 |
| 57 | 0.6224 | 0.7481 | 0.5870 | 0.6953 | 0.6399 | 0.7154 | 0.7487 | 0.7802 | 0.7863 | 0.7064 |
| 58 | 0.6167 | 0.7440 | 0.5805 | 0.6921 | 0.6352 | 0.6970 | 0.7423 | 0.7795 | 0.7895 | 0.7724 |
| 59 | 0.6055 | 0.7367 | 0.5678 | 0.6850 | 0.6258 | 0.6458 | 0.7296 | 0.7764 | 0.7891 | 0.7889 |
| 60 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |

N-P: n-pentane; N-H: n-hexane; 2-MB: 2-methyl butane; 2-MP: 2-methyl pentane; C-2-HE: cis-2-hexene; MCP: Methylcyclopentane; BZ: benzene; TOL: Toluene; OX: *o*-xylene; TMS: sulfolane

Now murphree efficiencies obtained from ChemSep are incorporated in ASPEN PLUS flow sheet extractive distillation column.

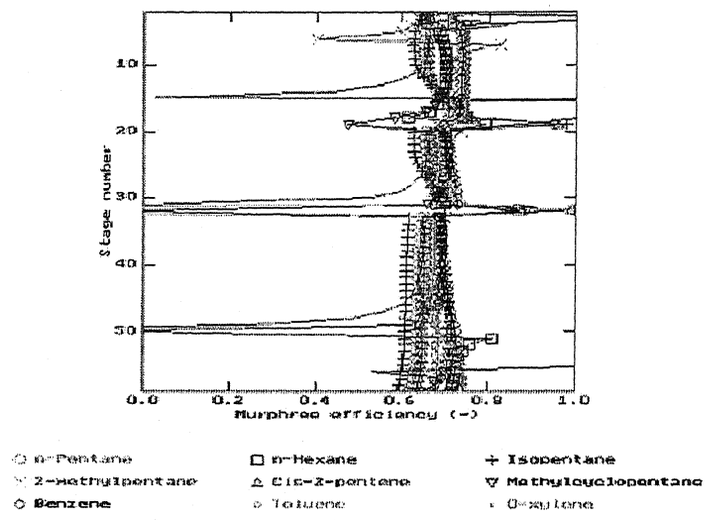
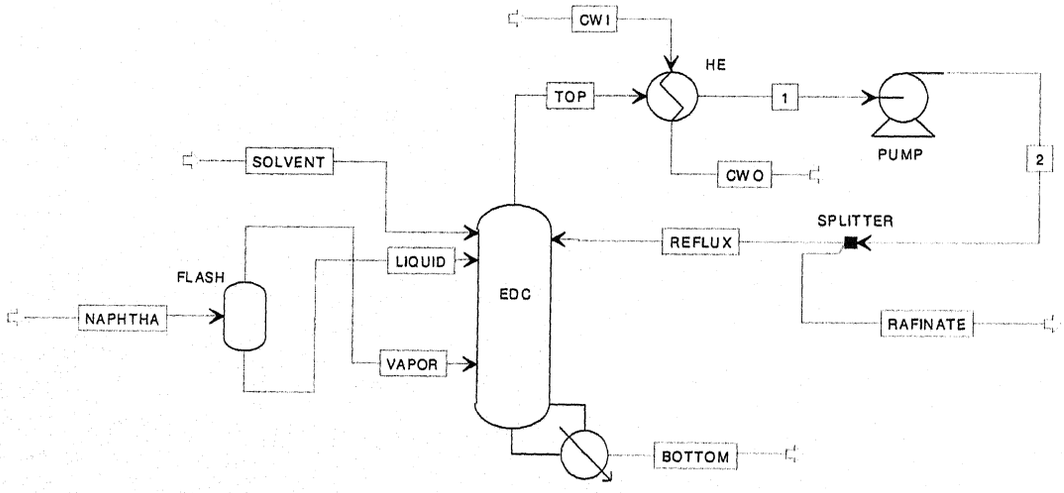



Figure 6.4 Murphree efficiency plot for extractive distillation column.

### 6.2.4 Simulation results

Flowsheet 6.1 shows the simulation flowsheet for extractive distillation column in ASPEN PLUS. Table 6.6 shows the simulation stream results and Table 6.7 shows the overall mass and energy balance results.




Flowsheet 6.1 Simulation flowsheet for extractive distillation column

Table 6.6 Simulation stream results for extractive distillation column before optimization

| Stream | BOTTOM | LIQUID | NAPHTHA | RAFINATE | REFLUX | SOLVENT | TOP | VAPOR |
|---|---|---|---|---|---|---|---|---|
| To | | EDC | FLASH | | EDC | EDC | HE | EDC |
| From | EDC | FLASH | | SPLITTER | SPLITTER | | EDC | FLASH |
| State | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | VAPOR | VAPOR |
| Mass Flow tonne/day | | | | | | | | |
| n-Pentane | 0.000 | 17.400 | 29.720 | 29.720 | 143.229 | 0.000 | 172.949 | 12.320 |
| n-Hexane | 0.000 | 42.368 | 54.920 | 54.920 | 264.675 | 0.000 | 319.595 | 12.552 |
| Iso-Pentane | 0.000 | 14.410 | 25.820 | 25.820 | 124.434 | 0.000 | 150.254 | 11.410 |
| 2-Methyl pentane | 0.000 | 96.665 | 130.180 | 130.180 | 627.374 | 0.000 | 757.554 | 33.515 |
| Cis-2-Hexene | 0.000 | 5.366 | 6.790 | 6.790 | 32.723 | 0.000 | 39.513 | 1.424 |
| Methylcyclopentane | **1.200** | 10.991 | 13.490 | 12.292 | 59.238 | 0.000 | 71.528 | 2.499 |
| Benzene | 284.742 | 251.714 | 299.970 | **15.227** | 73.380 | 0.000 | 88.608 | 48.256 |
| Toluene | 85.820 | 79.961 | 85.820 | 0.000 | 0.000 | 0.000 | 0.000 | 5.859 |
| *o*-Xylene | 3.290 | 3.202 | 3.290 | 0.000 | 0.000 | 0.000 | 0.000 | 0.088 |
| Sulfolane | 1275.000 | 0.000 | 0.000 | 0.000 | 0.000 | 1275.000 | 0.000 | 0.000 |
| water | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Total Flow kmol/hr | 634.653 | 265.374 | 331.718 | 139.139 | 670.551 | 442.075 | 809.691 | 66.344 |
| Total Flow tonne/day | 1650.052 | 522.078 | 650.000 | 274.948 | 1325.052 | 1275.000 | 1600.000 | 127.922 |
| Total Flow cum/hr | 66.885 | 30.599 | 36.911 | 18.371 | 88.535 | 42.596 | 15989.510 | 968.968 |
| Temperature C | 148.038 | 91.229 | 60.000 | 63.450 | 63.450 | 40.000 | 69.278 | 91.229 |
| Pressure kg/sqcm | 1.900 | 2.000 | 7.138 | 2.000 | 2.000 | 2.000 | 1.400 | 2.000 |
| Vapor Frac | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 1.000 | 1.000 |
| Liquid Frac | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 0.000 | 0.000 |
| Enthalpy kcal/kg | -603.379 | -86.682 | -130.062 | -490.810 | -490.811 | -874.620 | -408.002 | -147.290 |
| Enthalpy MMkcal/hr | -41.484 | -1.886 | -3.523 | -5.623 | -27.098 | -46.465 | -27.201 | -0.785 |
| Entropy cal/gm-K | -0.906 | -1.027 | -1.111 | -1.642 | -1.642 | -1.113 | -1.399 | -1.005 |
| Density kg/cum | 1027.920 | 710.920 | 733.756 | 623.605 | 623.605 | 1247.198 | 4.169 | 5.501 |
| Average MW | 108.331 | 81.972 | 81.646 | 82.336 | 82.336 | 120.172 | 82.336 | 80.341 |
| Liq Vol 60F cum/hr | 59.891 | 27.719 | 35.004 | 17.228 | 83.027 | 42.115 | 100.255 | 7.285 |

Table 6.7 Overall flowsheet balance of extractive distillation column

| Mass and Energy balance | | | |
|---|---|---|---|
| | In | Out | Relative difference |
| Mole, kmol/hr | 12384.300 | 12384.300 | 0.465738E-08 |
| Mass, tonne/day | 6945.000 | 6945.000 | 0.331334E-11 |
| Enthalpy, MMkcal/hr | -851.310 | -842.907 | -0.987080E-02 |

It has been observed that rich solvent stream, BOTTOM, contains 1.2 MT/D of methylcyclopentane and non-aromatic stream, RAFINATE, contains 15.227 MT/D of benzene, both of which should be minimized.

### 6.2.5 Sensitivity Analysis

Sensitivity analysis for dependent variables such as component flow rates in raffinate and rich solvent stream has been carried out with respect to most sensitive manipulated variables, distillate rate, reboiler duty and split fraction for the determination of sensitivity parameter $s$, where $s$ is defined as,

$$s_{ij} = \left| \left( \frac{\partial y_i}{\partial x_j} \right) \times \left( \frac{x_j}{y_i} \right) \right| \text{ at operating point} \qquad (6.1)$$

Where, $x_j$ and $y_i$ are respectively manipulated variables and dependent variables.

Table 6.8 Sensitivity parameter and sensitivity index for extractive distillation column

| Component flow rate, MT/D | | | Manipulated variable | | | Sensitivity index, $W_i = \sum S_{ij}$ |
|---|---|---|---|---|---|---|
| Block → | | | EDC | EDC | SPLIT | |
| Component | Stream | Sensitivity parameter | Distillate rate, MT/D | Reboiler duty, MMkcal/hr | Split fraction, REFLUX | |
| n-Pentane | RAFINATE | $s_{1j}$ → | 0.00000 | 0.00000 | 0.00593 | 0.00593 |
| n-Hexane | RAFINATE | $s_{2j}$ | 0.00004 | 0.00000 | 0.00599 | 0.00603 |
| Iso-Pentane | RAFINATE | $s_{3j}$ | 0.00000 | 0.00000 | 0.00593 | 0.00593 |
| 2-Methyl pentane | RAFINATE | $s_{4j}$ | 0.00000 | 0.00000 | 0.00593 | 0.00593 |
| Cis-2-Hexene | RAFINATE | $s_{5j}$ | 0.00438 | 0.00003 | 0.01398 | 0.01840 |
| Methylcyclopentane | RAFINATE | $s_{6j}$ | **10.29122** | **0.63933** | **42.17447** | **53.10503** |
| Benzene | BOTTOM | $s_{7j}$ | **0.52088** | **0.02763** | **2.83001** | **3.37852** |
| Toluene | BOTTOM | $s_{8j}$ | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| *o*-Xylene | BOTTOM | $s_{9j}$ | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| Sulfolane | BOTTOM | $s_{10j}$ | 0.00000 | 0.00000 | 0.00000 | 0.00000 |

Sensitivity parameters for same component flow and different manipulated variable are added to get sensitivity index, $W_i$. Sensitivity parameter and sensitivity index for different dependent variables are given in Table 6.8. These sensitivity indexes are used in optimization. It is found that methylcyclopentane flow in raffinate and benzene in rich solvent stream are highly sensitive to manipulated variables.

### 6.2.6 Optimization

6.2.6.1 Formulation of objective function

Optimization tool is used to minimize aromatics in raffinate and non-aromatics in rich solvent stream. An objective function, OBJ, is formulated and minimized using optimization tool. Objective function as used is as follows,

P1=0.0059269*((NPF-NPN)/NPF)*((NPF-NPN)/NPF)

P2=0.006031045*((NHF-NHN)/NHF)*((NHF-NHN)/NHF)

I1=0.005926656*((MB2F-MB2N)/MB2F)*((MB2F-MB2N)/MB2F)

I2=0.005926471*((MP2F-MP2N)/MP2F)*((MP2F-MP2N)/MP2F)

O=0.018401121*((C2HF-C2HN)/C2HF)*((C2HF-C2HN)/C2HF)

N=53.10502772*((MCPF-MCPN)/MCPF)*((MCPF-MCPN)/MCPF)

A1=3.378518693*((BZF-BZB)/BZF)*((BZF-BZB)/BZF)

A2=0.00000044158103995 5857*((TOLF-TOLB)/TOLF)*((TOLF-TOLB)/TOLF)

A3=0*((OXF-OXB)/OXF)*((OXF-OXB)/OXF)

S=0*((TMSF-TMSB)/TMSF)*((TMSF-TMSB)/TMSF)

P=P1+P2

I=I1+I2

A=A1+A2+A3

OBJ=P+I+O+N+A+S

Where NPF, NHF, MB2F, MP2F, C2HF, MCPF, BZF, TOLF, OXF respectively stands for n-pentane, n-hexane, 2-methyl butane, 2-methyl pentane, cis-2-hexene, methylcyclopentane, benzene, toluene and *o*-xylene flow rate in naphtha feed, TMSF stands for sulfolane flow rate in solvent feed, NPN, NHN, MB2N, MP2N, C2HN, MCPN respectively stands for n-pentane, n-hexane, 2-methyl butane, 2-methyl pentane, cis-2-

hexene and methylcyclopentane flow rate in raffinate and BZB, TOLB, OXB and TMSB respectively stands for benzene, toluene and sulfolane flow rate in rich solvent stream. FORTRAN statement has been used for above formulation. Distillate rate and reboiler duty of extractive distillation column, EDC, and split fraction of splitter, SPLIT, are used as manipulated variable. Sequential Quadratic Programming (SQP) algorithm is used for optimization. ASPEN PLUS input summary is given in Appendix C.1.

6.2.6.2 Optimization results

Final value of manipulated variables is given in Table 6.9.

Table 6.9 Manipulated variables after optimization for extractive distillation column

| Block | Variable | Initial value | Limits | | Final value |
|---|---|---|---|---|---|
| | | | Lower | Upper | |
| EDC | Distillate rate, MT/D | 1600.0000 | 1570.0000 | 1630.0000 | 1620.0224 |
| EDC | Reboiler duty, MMkcal/hr | 20.0000 | 17.0000 | 23.0000 | 18.8131 |
| SPLIT | Split fraction, REFLUX | 0.82816 | 0.80000 | 0.84000 | 0.82845 |

Optimization stream results are given in Table 6.10. Now methylcyclopentane in solvent rich stream, BOTTOM, is reduced from 1.2 MT/D to 0.308 MT/D and flow rate of benzene in raffinate, RAFINATE, is increased from 15.227 MT/D to 17.296 MT/D. Thus we will get more pure aromatics at the cost some production loss.

**6.2.7 Discussion**

As shown in Figure 6.5, the temperature changes most rapidly at the very top, at the bottom of the column, and in the vicinity of the lean solvent point and the feed point of the extractive distillation. The temperature profiles inside the column, the temperatures at the reboiler and condenser, are 148.42 °C and 69.43 °C, respectively. The pressure increases gradually toward bottom of the column. Considering Figure 6.6 and Figure 6.7, above the feed benzene in both liquid and vapor dies out rapidly. Because of low relative volatility with response to all other components present, this component does not enter the up flowing vapor on the stages above the feed to any large extent. While above the feed n-hexane and 2-methyl pentane in both liquid and vapor increases rapidly till feed stage of lean solvent. In 1 to 3 stages occurs vapor-$2^{nd}$ liquid phase, 4 to 19 vapor-$1^{st}$ liquid-$2^{nd}$ liquid and 20-60 stages vapor-$1^{st}$ liquid phase. The $1^{st}$ liquid phase contains sulfolane and aromatics to be highly soluble in sulfolane. The $2^{nd}$ liquid contains non-aromatics.

Table 6.10 Simulation stream results for extractive distillation column after optimization.

| Stream | BOTTOM | LIQUID | NAPHTHA | RAFINATE | REFLUX | SOLVENT | TOP | VAPOR |
|---|---|---|---|---|---|---|---|---|
| To | | EDC | FLASH | | EDC | EDC | HE | EDC |
| From | EDC | FLASH | | SPLITTER | SPLITTER | | EDC | FLASH |
| State | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | VAPOR | VAPOR |
| Mass Flow tonne/day | | | | | | | | |
| n-Pentane | 0.000 | 17.400 | 29.720 | 29.720 | 143.527 | 0.000 | 173.247 | 12.320 |
| n-Hexane | 0.000 | 42.368 | 54.920 | 54.920 | 265.226 | 0.000 | 320.146 | 12.552 |
| Iso-Pentane | 0.000 | 14.410 | 25.820 | 25.820 | 124.693 | 0.000 | 150.513 | 11.410 |
| 2-Methyl pentane | 0.000 | 96.665 | 130.180 | 130.180 | 628.681 | 0.000 | 758.861 | 33.515 |
| Cis-2-Hexene | 0.000 | 5.366 | 6.790 | 6.790 | 32.791 | 0.000 | 39.581 | 1.424 |
| Methylcyclopentane | **0.308** | 10.991 | 13.490 | 13.184 | 63.670 | 0.000 | 76.852 | 2.499 |
| Benzene | 282.669 | 251.714 | 299.970 | **17.296** | 83.521 | 0.000 | 100.822 | 48.256 |
| Toluene | 85.820 | 79.961 | 85.820 | 0.000 | 0.000 | 0.000 | 0.000 | 5.859 |
| *o*-Xylene | 3.290 | 3.202 | 3.290 | 0.000 | 0.000 | 0.000 | 0.000 | 0.088 |
| Sulfolane | 1275.000 | 0.000 | 0.000 | 0.000 | 0.000 | 1275.000 | 0.000 | 0.000 |
| water | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Total Flow kmol/hr | 633.105 | 265.374 | 331.718 | 140.685 | 679.409 | 442.075 | 820.096 | 66.344 |
| Total Flow tonne/day | 1647.086 | 522.078 | 650.000 | 277.909 | 1342.109 | 1275.000 | 1620.022 | 127.922 |
| Total Flow cum/hr | 66.736 | 30.599 | 36.911 | 18.531 | 89.492 | 42.596 | 16204.340 | 968.968 |
| Temperature C | 148.423 | 91.229 | 60.000 | 63.596 | 63.596 | 40.000 | 69.435 | 91.229 |
| Pressure kg/sqcm | 1.900 | 2.000 | 7.138 | 2.000 | 2.000 | 2.000 | 1.400 | 2.000 |
| Vapor Frac | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 1.000 | 1.000 |
| Liquid Frac | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 0.000 | 0.000 |
| Enthalpy kcal/kg | -604.381 | -86.682 | -130.062 | -485.426 | -485.428 | -874.620 | -402.540 | -147.290 |
| Enthalpy MMkcal/hr | -41.478 | -1.886 | -3.523 | -5.621 | -27.146 | -46.465 | -27.172 | -0.785 |
| Entropy cal/gm-K | -0.906 | -1.027 | -1.111 | -1.634 | -1.634 | -1.113 | -1.390 | -1.005 |
| Density kg/cum | 1028.361 | 710.920 | 733.756 | 624.873 | 624.873 | 1247.198 | 4.166 | 5.501 |
| Average MW | 108.400 | 81.972 | 81.646 | 82.309 | 82.309 | 120.172 | 82.309 | 80.341 |
| Liq Vol 60F cum/hr | 59.744 | 27.719 | 35.004 | 17.375 | 83.910 | 42.115 | 101.285 | 7.285 |

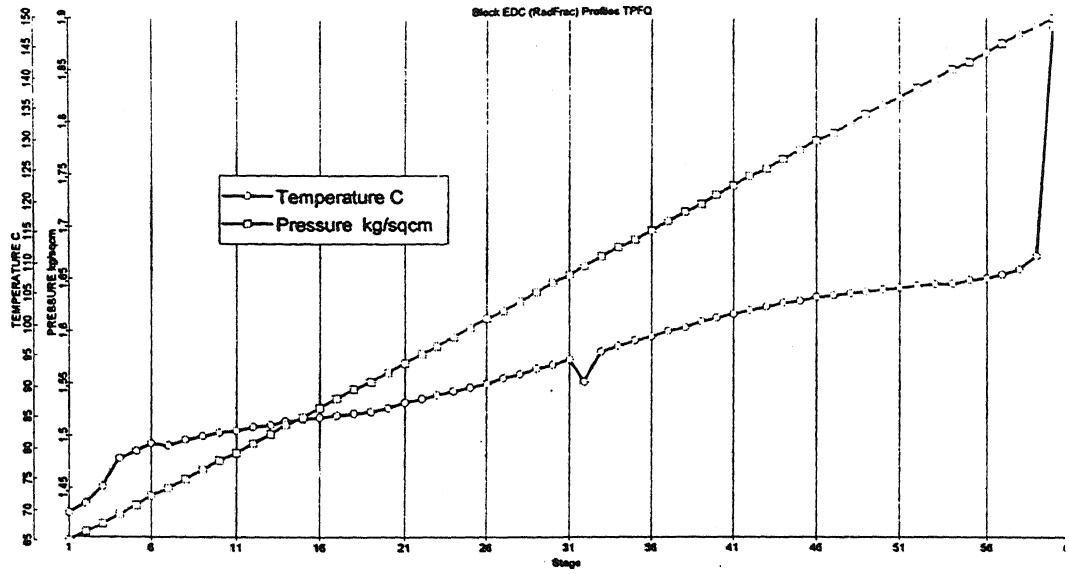



Figure 6.5 Temperature and pressure profile in extractive distillation column.

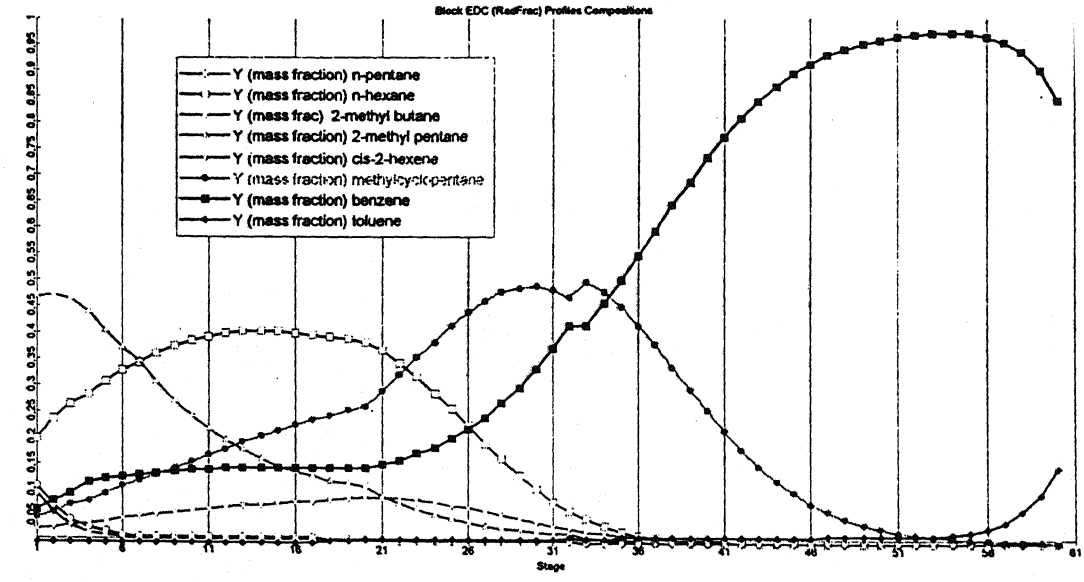



Figure 6.6 Vapor-composition profiles in extractive distillation column.

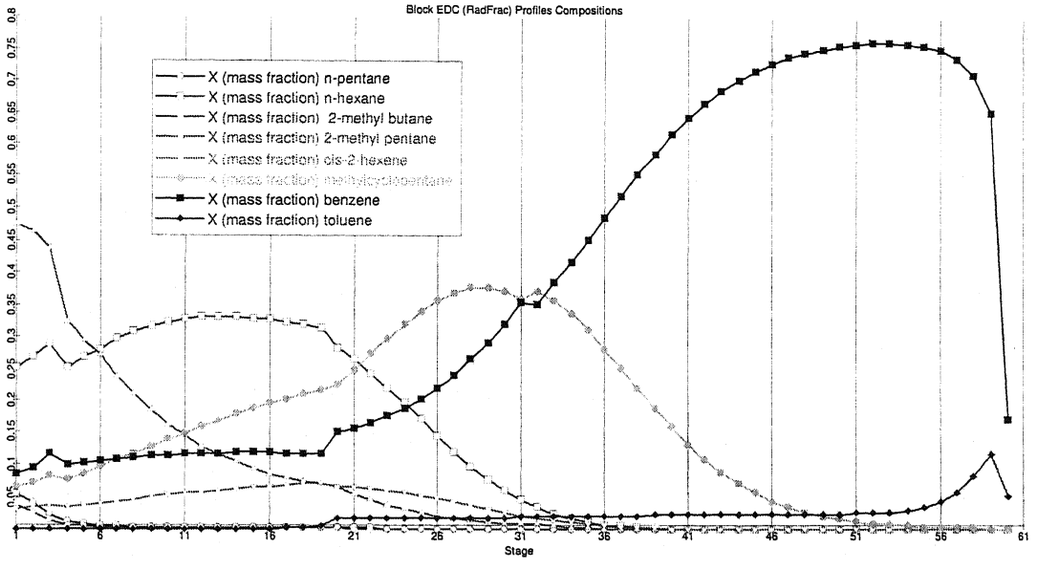



Figure 6.7 Liquid-composition profiles in extractive distillation column.

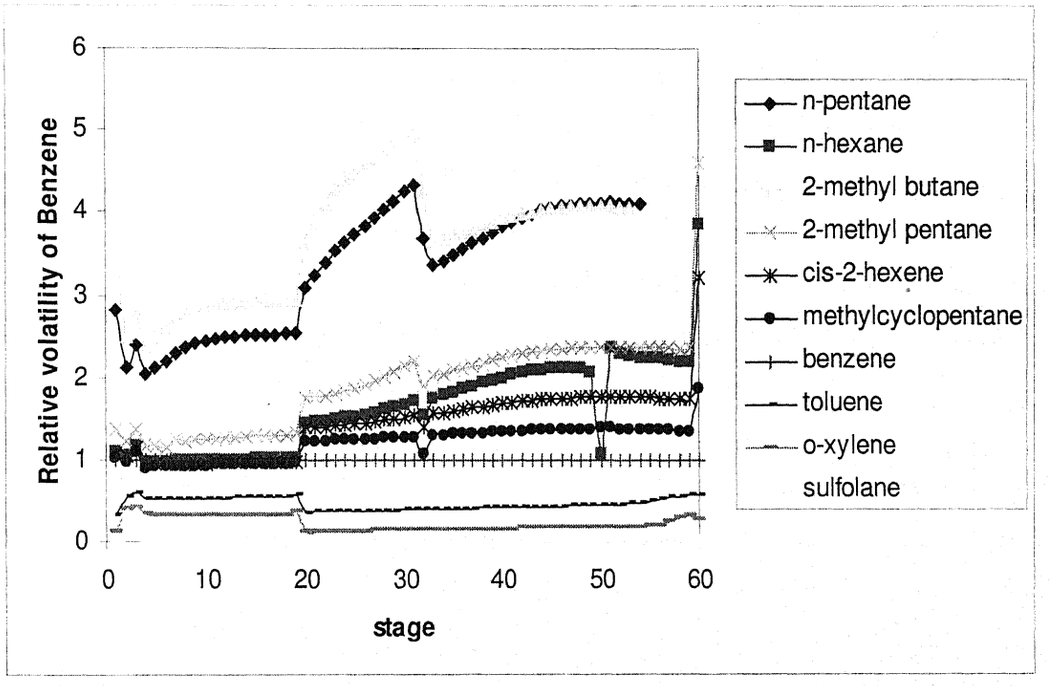



Figure 6.8 Relative volatility profiles in extractive distillation column.

Figure 6.8 shows the relative volatility on the basis of the benzene. The relative volatility is less for the benzene than for non-aromatics and more than for other aromatics and sulfolane, because of the difference of the mutual solubility among aromatics, non-aromatics and sulfolane.

## 6.3 Simulation of complete Aromatic Recovery Unit

### 6.3.1 Input Specifications

Solvent recovery column, benzene column and toluene column are simulated individually before attempt was made to complete the whole flowsheet. Input specifications for solvent recovery column, benzene column and toluene column are given in Table 6.11. Same specifications as used in chapter 4 have been used, except streams and distillate to feed ratio of solvent recovery column, which is modified according to present feed to the column.

### 6.3.2 Property method

RK-SOAVE property method is used in solvent recovery column, benzene column and toluene column.

### 6.3.3 Efficiencies

Input Specifications for ChemSep simulation is given in Table 6.12. Murphree efficiency for solvent recovery column, benzene column and toluene column calculated from ChemSep are reported respectively in Table 6.13-6-15. Efficiency plot as obtained from ChemSep are shown in Figure C.1-C.3 of Appendix C.

### 6.3.4 Flowsheet connectivity and calculation sequence

After changing the distillate rate and reboiler duty of extractive distillation column, EDC, and split fraction of splitter, SPLIT, to its optimum value we starts adding solvent recovery column, benzene column and toluene column one by one. Complete aromatic recovery unit (ARU) flowsheet is shown in Flowsheet 6.2. Recycle streams in the complete ARU flow sheet are external reflux stream, REFLUX, to extractive distillation column, EDC, external reflux stream, RFLX, to solvent recovery column, SRC, and lean recycle solvent stream, SOLVENT, to extractive distillation column. Both the external reflux recycle streams are independent and are nested to lean solvent recycle stream.

Table 6.11 Specifications of other columns for extractive distillation aromatic recovery unit

| Column Specifications | | | | | |
|---|---|---|---|---|---|
| **Solvent Recovery Column** | | **Benzene Column** | | **Toluene Column** | |
| **Configuration** | | **Configuration** | | **Configuration** | |
| Number of stages | 35 | Number of Stages | 43 | Number of Stages | 50 |
| Condenser | None | Condenser | Total | Condenser | Total |
| Reboiler | Kettle | Reboiler | Kettle | Reboiler | Kettle |
| Valid phases | Vapor-liquid | Valid phases | Vapor-Liquid | Valid phases | Vapor-Liquid |
| Convergence | Standard | Convergence | Standard | Convergence | Standard |
| Distillate to feed ratio | 0.3659 | Reflux rate, MT/D | 609.000 | Reflux rate, MT/D | 75.400 |
| | | Boilup ratio, mole | 7.3831 | Boilup ratio, mole | 50.2700 |
| **Streams** | | **Streams** | | **Streams** | |
| Reflux | 1 | Benzene Drag | 1 | Toluene Product | 1 |
| Water Feed | 4 | Benzene Product | 5 | Feed | 22 |
| Bottom Feed | 21 | Feed | 27 | Bottom Product | 50 |
| Top Vapor Product | 1 | Bottom Product | 43 | | |
| Solvent Product | 35 | | | | |
| **Column type** | | **Column type** | | **Column type** | |
| 1 to 34 | Sieve Trays | 2 to 26 | Structured packing[a] | 2 to 21 | Structured packing[a] |
| | | 27 to 42 | Structured packing[a] | 22 to 49 | Structured packing[a] |
| **Block options** | | **Block options** | | **Block options** | |
| Property method | RK-SOAVE | Property method | RK-SOAVE | Property method | RK-SOAVE |
| **Pressure**, kg/sqcm | | **Pressure** | | **Pressure** | |
| Top pressure | 0.56 | Top pressure | 0.47 kg/sqcmg | Top pressure | 0.20 kg/sqcmg |
| Pressure drop | 0.07 | Pressure drop | 487 mm-water | Pressure drop | 555 mm-water |
| **Convergence** | | **Convergence** | | **Convergence** | |
| Algorithm | Standard | Algorithm | Standard | Algorithm | Standard |
| Tears | Broyden | Tears | Broyden | Tears | Broyden |
| Type: MELLAPAK, Vendor: SULZER, Size: 250X | | | | | |

Table 6.12 ChemSep input specifications of other columns for extractive distillation aromatic recovery unit

| Specifications | Solvent Recovery Column | Benzene Column | Toluene Column |
|---|---|---|---|
| Operation | NonEquilibrium | NonEquilibrium | NonEquilibrium |
| Type | Simple Distillation | Simple Distillation | Simple Distillation |
| Column internals | Sieve tray | Structured packing | Structured packing |
| Section height, m | n.a. | 19.458, 13.536 | 14.934, 21.222 |
| Column diameter, m | 3.000 | 2.200 | 0.800 |
| Packing type | n.a. | Sulzer BX | Sulzer BX |
| Tray spacing, m | 0.800 | | |
| Number of flow passes | 1 | | |
| Liquid flow path length, m | 1.600 | | |
| Downcomer clearance, m | 0.0381 | | |
| Deck thickness, m | 0.00254 | | |
| Hole diameter, m | 0.005-0.012 | | |
| Hole pitch, m | 0.032 | | |
| Active area, % total | 60.000 | | |
| Total hole area, % active | 10.000 | | |
| Downcomer area, % total | 12.000 | | |
| Weir type | Segmental | | |
| Weir length, m | 2.100 | | |
| Weir height, m | 0.040 | | |

Table 6.13 Murphree efficiencies for solvent recovery column

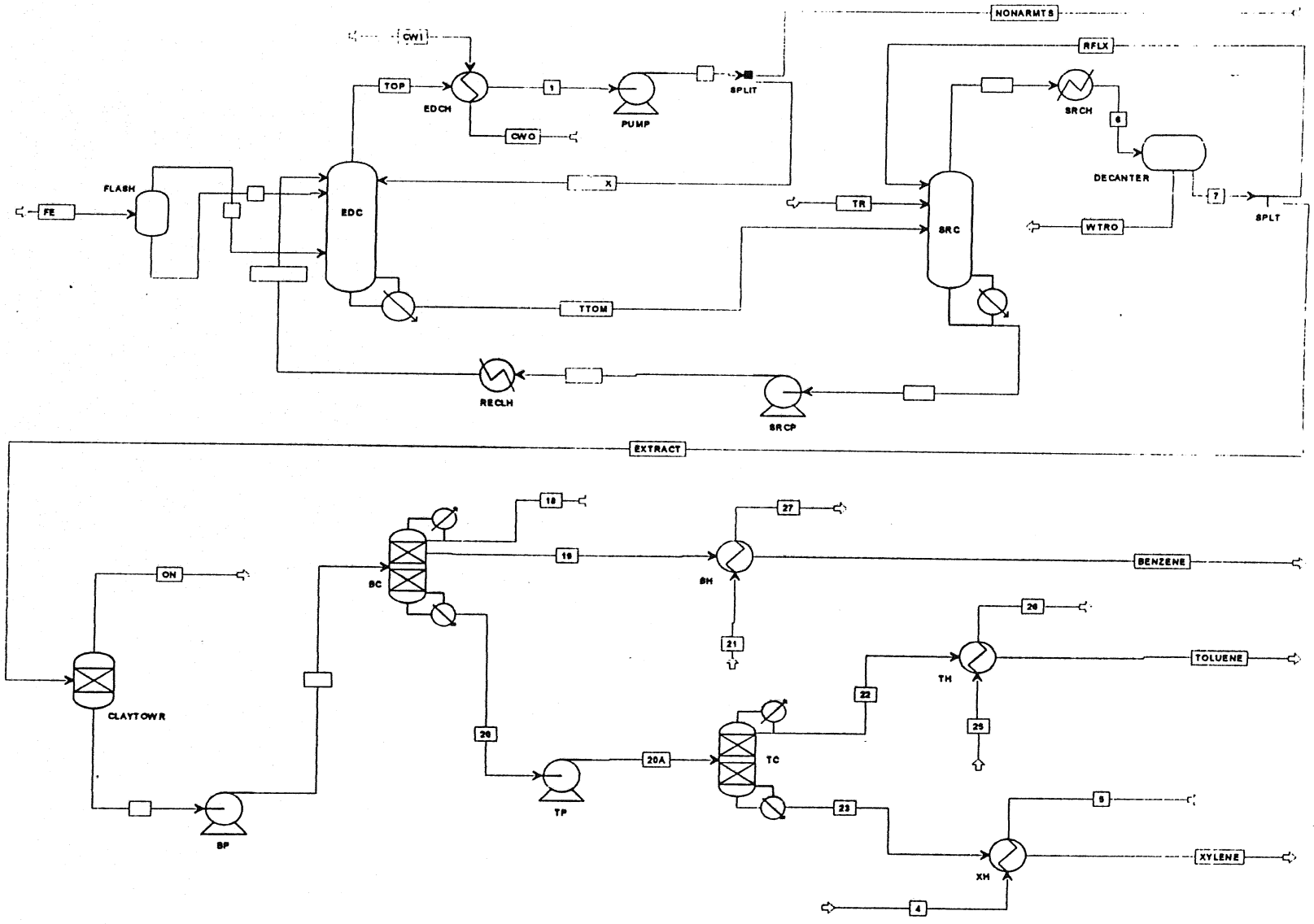
| Stage | BE | TOL | OX | TMS | Stage | BE | TOL | OX | TMS |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.5414 | 0.5462 | 0.5149 | 0.5095 | 19 | 0.4816 | 0.4659 | 0.4419 | 0.4784 |
| 2 | 0.4431 | 0.7336 | 0.4843 | 0.4938 | 20 | 0.4816 | 0.4660 | 0.4420 | 0.4784 |
| 3 | 0.5106 | 0.5076 | 0.5022 | 0.4939 | 21 | 0.9914 | 1.0000 | 1.0000 | 0.8672 |
| 4 | 0.4848 | 0.4851 | 0.4848 | 0.4859 | 22 | 0.5842 | 0.5669 | 0.6173 | 0.6549 |
| 5 | 0.4164 | 0.4398 | 0.4441 | 0.4616 | 23 | 0.5847 | 0.5426 | 0.6126 | 0.6571 |
| 6 | 0.3345 | 0.4520 | 0.4458 | 0.4631 | 24 | 0.5872 | 0.3979 | 0.5958 | 0.6581 |
| 7 | 0.4509 | 0.4447 | 0.4478 | 0.4236 | 25 | 0.5792 | 0.8188 | 0.4950 | 0.6475 |
| 8 | 0.4802 | 0.4706 | 1.0000 | 0.4785 | 26 | 0.5078 | 0.6107 | 0.9448 | 0.5729 |
| 9 | 0.4814 | 0.4664 | 0.4582 | 0.4779 | 27 | 0.3360 | 0.3999 | 0.5158 | 0.3910 |
| 10 | 0.4814 | 0.4664 | 0.4602 | 0.4777 | 28 | 0.2262 | 0.2734 | 0.3615 | 0.2747 |
| 11 | 0.4812 | 0.4673 | 0.4671 | 0.4754 | 29 | 0.1952 | 0.2373 | 0.3171 | 0.2444 |
| 12 | 0.4816 | 0.4653 | 0.5334 | 0.4789 | 30 | 0.1894 | 0.2303 | 0.3083 | 0.2423 |
| 13 | 0.4815 | 0.4658 | 0.4194 | 0.4785 | 31 | 0.1883 | 0.2290 | 0.3067 | 0.2464 |
| 14 | 0.4815 | 0.4659 | 0.4353 | 0.4785 | 32 | 0.1881 | 0.2287 | 0.3064 | 0.2517 |
| 15 | 0.4815 | 0.4659 | 0.4392 | 0.4784 | 33 | 0.1880 | 0.2287 | 0.3063 | 0.2573 |
| 16 | 0.4815 | 0.4659 | 0.4407 | 0.4784 | 34 | 0.1880 | 0.2287 | 0.3063 | 0.2629 |
| 17 | 0.4815 | 0.4659 | 0.4414 | 0.4784 | 35 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 18 | 0.4816 | 0.4659 | 0.4417 | 0.4784 | | | | | |

Table 6.14 Murphree efficiencies for benzene column

| Stage | BE | TOL | OX | Stage | BE | TOL | OX |
|---|---|---|---|---|---|---|---|
| 1 | 1.0000 | 1.0000 | 1.0000 | 23 | 0.8130 | 0.8101 | 0.8219 |
| 2 | 0.8200 | 0.8200 | 0.8194 | 24 | 0.8128 | 0.7913 | 0.8219 |
| 3 | 0.8201 | 0.8201 | 0.8193 | 25 | 0.9989 | 1.0000 | 0.6086 |
| 4 | 0.8201 | 0.8201 | 0.8194 | 26 | 0.8308 | 0.8308 | 0.8262 |
| 5 | 0.8202 | 0.8202 | 0.8196 | 27 | 0.8286 | 0.8286 | 0.8243 |
| 6 | 0.8202 | 0.8202 | 0.8199 | 28 | 0.8268 | 0.8268 | 0.8227 |
| 7 | 0.8202 | 0.8202 | 0.8202 | 29 | 0.8256 | 0.8256 | 0.8217 |
| 8 | 0.8201 | 0.8201 | 0.8206 | 30 | 0.8247 | 0.8247 | 0.8212 |
| 9 | 0.8198 | 0.8198 | 0.8210 | 31 | 0.8242 | 0.8242 | 0.8214 |
| 10 | 0.8192 | 0.8192 | 0.8213 | 32 | 0.8239 | 0.8239 | 0.8233 |
| 11 | 0.8184 | 0.8184 | 0.8215 | 33 | 0.8238 | 0.8237 | 0.8277 |
| 12 | 0.8174 | 0.8174 | 0.8216 | 34 | 0.8237 | 0.8236 | 0.8323 |
| 13 | 0.8164 | 0.8164 | 0.8216 | 35 | 0.8236 | 0.8234 | 0.8346 |
| 14 | 0.8155 | 0.8155 | 0.8217 | 36 | 0.8236 | 0.8226 | 0.8354 |
| 15 | 0.8148 | 0.8148 | 0.8217 | 37 | 0.8236 | 0.8189 | 0.8356 |
| 16 | 0.8142 | 0.8142 | 0.8217 | 38 | 0.8235 | 1.0000 | 0.8357 |
| 17 | 0.8138 | 0.8138 | 0.8218 | 39 | 0.8235 | 0.8397 | 0.8357 |
| 18 | 0.8137 | 0.8137 | 0.8219 | 40 | 0.8235 | 0.8366 | 0.8357 |
| 19 | 0.8135 | 0.8135 | 0.8219 | 41 | 0.8235 | 0.8360 | 0.8358 |
| 20 | 0.8133 | 0.8133 | 0.8219 | 42 | 0.8236 | 0.8360 | 0.8359 |
| 21 | 0.8132 | 0.8130 | 0.8219 | 43 | 1.0000 | 1.0000 | 1.0000 |
| 22 | 0.8131 | 0.8124 | 0.8219 | | | | |

Table 6.15 Murphree efficiencies for toluene column

| Stage | TOL | OX | Stage | TOL | OX | Stage | TOL | OX |
|---|---|---|---|---|---|---|---|---|
| 1 | 1.0000 | 1.0000 | 18 | 1.0000 | 0.9211 | 35 | 0.8189 | 0.8189 |
| 2 | 0.7834 | 0.7834 | 19 | 0.8594 | 0.8187 | 36 | 0.8189 | 0.8189 |
| 3 | 0.7833 | 0.7833 | 20 | 0.8196 | 0.8170 | 37 | 0.8189 | 0.8189 |
| 4 | 0.7833 | 0.7833 | 21 | 1.0000 | 1.0000 | 38 | 0.8189 | 0.8189 |
| 5 | 0.7833 | 0.7833 | 22 | 0.8189 | 0.8189 | 39 | 0.8189 | 0.8189 |
| 6 | 0.7833 | 0.7833 | 23 | 0.8189 | 0.8189 | 40 | 0.8189 | 0.8189 |
| 7 | 0.7833 | 0.7833 | 24 | 0.8189 | 0.8189 | 41 | 0.8190 | 0.8190 |
| 8 | 0.7833 | 0.7833 | 25 | 0.8189 | 0.8189 | 42 | 0.8190 | 0.8190 |
| 9 | 0.7833 | 0.7833 | 26 | 0.8189 | 0.8189 | 43 | 0.8191 | 0.8191 |
| 10 | 0.7832 | 0.7836 | 27 | 0.8189 | 0.8189 | 44 | 0.8194 | 0.8194 |
| 11 | 0.7826 | 0.7866 | 28 | 0.8189 | 0.8189 | 45 | 0.8198 | 0.8198 |
| 12 | 0.7660 | 0.8200 | 29 | 0.8189 | 0.8189 | 46 | 0.8204 | 0.8204 |
| 13 | 0.6000 | 1.0000 | 30 | 0.8189 | 0.8189 | 47 | 0.8210 | 0.8210 |
| 14 | 0.0001 | 0.0001 | 31 | 0.8189 | 0.8189 | 48 | 0.8208 | 0.8208 |
| 15 | 0.0001 | 0.0336 | 32 | 0.8189 | 0.8189 | 49 | 0.8188 | 0.8188 |
| 16 | 0.0001 | 0.3696 | 33 | 0.8189 | 0.8189 | 50 | 1.0000 | 1.0000 |
| 17 | 1.0000 | 1.0000 | 34 | 0.8189 | 0.8189 | | | |




Flowsheet 6.2 Simulation flowsheet of extractive distillation aromatic recovery unit

Convergence sequence used for complete ARU flowsheet simulation is given below,

FLASH
C-3
| C-1 EDC EDCH PUMP SPLIT
| (RETURN C-1)
| C-2 SRC SRCH DECANTER SPLT
| (RETURN C-2)
| SRCP RECLH
(RETURN C-3)
CLAYTOWR BP BC TP TC TH XH BH

Where C-1, C-2 and C-3 are user defined convergence block respectively used external reflux stream, REFLUX, to extractive distillation column, EDC, external reflux stream, RLFX, to solvent recovery column, SRC, and lean solvent recycle stream ,SOLVENT, to extractive distillation column as tear stream. User defined convergence block input and convergence order form are shown respectively in Figure C.4 and Figure C.5 of Appendix C.

### 6.3.5 Simulation results

End products purity is given in Table 6.16. Simulation stream results of complete aromatic recovery unit are reported in Table 6.17.

Table 6.16 Product purity for extractive distillation aromatic recovery unit.

| Description | Stream | Simulation result |
|---|---|---|
| Aromatics in non aromatics product | NONARMTS | 6.200 %, Mass |
| Non aromatics in benzene product | BENZENE | 3.000 PPM |
| Toluene in benzene product | BENZENE | 255.000 PPM |
| Xylene in benzene product | BENZENE | 0.000 PPM |
| Non aromatics in toluene product | TOLUENE | 0.000 PPM |
| Benzene in toluene product | TOLUENE | 266.000 PPM |
| Xylene in toluene product | TOLUENE | 298.000 PPM |
| Non aromatics in Xylene | XYLENE | 0.000 PPM |
| Benzene in Xylene product | XYLENE | 0.000 PPM |
| Toluene in Xylene | XYLENE | 263.000 PPM |

### 6.3.6 Performance index

Performance index (*PI*) as defined in Chapter 4 has been used to evaluate the performance of complete aromatic recovery unit with extractive distillation.

Table 6.17 Simulation stream results for extractive distillation aromatic recovery unit

| Stream | 1 | 2 | 4 | 5 | 6 | 7 | 13 | 16A |
|---|---|---|---|---|---|---|---|---|
| To | PUMP | SPLIT | XH | | DECANTER | SPLT | BP | BC |
| From | EDCH | PUMP | | XH | SRCH | DECANTER | CLAYTOWR | BP |
| State | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID |
| Mass Flow tonne/day | | | | | | | | |
| n-Pentane | 173.244 | 173.244 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| n-Hexane | 320.136 | 320.136 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Iso-Pentane | 150.506 | 150.506 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 2-Methyl pentane | 758.836 | 758.836 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Cis-2-Hexene | 39.573 | 39.573 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Methylcyclopentane | 76.880 | 76.880 | 0.000 | 0.000 | 0.372 | 0.372 | 0.001 | 0.001 |
| Benzene | 100.848 | 100.848 | 0.000 | 0.000 | 343.449 | 343.449 | 280.000 | 280.000 |
| Toluene | 0.000 | 0.000 | 0.000 | 0.000 | 104.271 | 104.271 | 85.820 | 85.820 |
| *o*-Xylene | 0.000 | 0.000 | 0.000 | 0.000 | 3.997 | 3.997 | 3.290 | 3.290 |
| Sulfolane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| water | 0.000 | 0.000 | 6.000 | 6.000 | 10.001 | 0.003 | 0.000 | 0.000 |
| Total Flow kmol/hr | 820.097 | 820.097 | 13.877 | 13.877 | 255.235 | 232.113 | 189.456 | 189.456 |
| Total Flow tonne/day | 1620.022 | 1620.022 | 6.000 | 6.000 | 462.091 | 452.093 | 369.111 | 369.111 |
| Total Flow cum/hr | 108.016 | 108.023 | 0.252 | 0.258 | 22.749 | 22.026 | 19.531 | 19.533 |
| Temperature C | 63.557 | 63.596 | 25.000 | 50.433 | 59.227 | 40.000 | 104.100 | 104.153 |
| Pressure kg/sqcm | 1.400 | 2.000 | 1.033 | 1.033 | 0.560 | 1.033 | 1.033 | 1.600 |
| Vapor Frac | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Liquid Frac | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Enthalpy kcal/kg | -485.445 | -485.413 | -3832.114 | -3802.777 | 54.158 | 126.501 | 154.661 | 154.694 |
| Enthalpy Btu/hr | -1.300E+08 | -1.300E+08 | -3.802E+06 | -3.773E+06 | 4.138E+06 | 9.456E+06 | 9.439E+06 | 9.441E+06 |
| Entropy cal/gm-K | -1.634 | -1.634 | -2.270 | -2.175 | -0.757 | -0.768 | -0.687 | -0.687 |
| Density kg/cum | 624.918 | 624.877 | 993.515 | 968.645 | 846.349 | 855.234 | 787.437 | 787.377 |
| Average MW | 82.309 | 82.309 | 18.015 | 18.015 | 75.436 | 81.156 | 81.178 | 81.178 |
| Liq Vol 60F cum/hr | 101.285 | 101.285 | 0.250 | 0.250 | 21.836 | 21.419 | 17.485 | 17.485 |

*(continued on next page)*

| Stream | 18 | 19 | 20 | 20A | 21 | 22 | 23 | 25 |
|---|---|---|---|---|---|---|---|---|
| To | | BH | TP | TC | BH | TH | XH | TH |
| From | BC | BC | BC | TP | | TC | TC | |
| State | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID |
| Mass Flow tonne/day | | | | | | | | |
| n-Pentane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| n-Hexane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Iso-Pentane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| 2-Methyl pentane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Cis-2-Hexene | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Methylcyclopentane | 0.000 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Benzene | 0.049 | 279.928 | 0.023 | 0.023 | 0.000 | 0.023 | 0.000 | 0.000 |
| Toluene | 0.000 | 0.071 | 85.749 | 85.749 | 0.000 | 85.748 | 0.001 | 0.000 |
| *o*-Xylene | 0.000 | 0.000 | 3.290 | 3.290 | 0.000 | 0.026 | 3.264 | 0.000 |
| Sulfolane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| water | 0.000 | 0.000 | 0.000 | 0.000 | 250.000 | 0.000 | 0.000 | 110.000 |
| Total Flow kmol/hr | 0.026 | 149.350 | 40.080 | 40.080 | 578.214 | 38.798 | 1.281 | 254.414 |
| Total Flow tonne/day | 0.049 | 280.000 | 89.061 | 89.061 | 250.000 | 85.796 | 3.265 | 110.000 |
| Total Flow cum/hr | 0.003 | 14.563 | 4.876 | 4.882 | 10.485 | 4.641 | 0.179 | 4.613 |
| Temperature C | 93.328 | 93.441 | 128.148 | 129.098 | 25.000 | 118.784 | 153.045 | 25.000 |
| Pressure kg/sqcm | 1.503 | 1.508 | 1.552 | 7.033 | 1.033 | 1.233 | 1.289 | 1.033 |
| Vapor Frac | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Liquid Frac | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Enthalpy kcal/kg | 179.132 | 179.160 | 73.588 | 74.137 | -3832.114 | 72.099 | 4.772 | -3832.114 |
| Enthalpy Btu/hr | 1.463E+03 | 8.295E+06 | 1.084E+06 | 1.092E+06 | -1.584E+08 | 1.023E+06 | 2.576E+03 | -6.970E+07 |
| Entropy cal/gm-K | -0.685 | -0.685 | -0.757 | -0.756 | -2.270 | -0.767 | -0.850 | -2.270 |
| Density kg/cum | 801.251 | 801.121 | 761.113 | 760.074 | 993.515 | 770.303 | 762.126 | 993.515 |
| Average MW | 78.114 | 78.117 | 92.588 | 92.588 | 18.015 | 92.140 | 106.163 | 18.015 |
| Liq Vol 60F cum/hr | 0.002 | 13.219 | 4.263 | 4.263 | 10.437 | 4.109 | 0.154 | 4.592 |

*(continued on next page)*

| Stream | 26 | 27 | BENZENE | BOTTOM | CWI | CWO | EXTRACT | FEED |
|---|---|---|---|---|---|---|---|---|
| To | | | | SRC | EDCH | | CLAYTOWR | FLASH |
| From | TH | BH | BH | EDC | | EDCH | SPLT | |
| State | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID |
| Mass Flow tonne/day | | | | | | | | |
| n-Pentane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 29.720 |
| n-Hexane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 54.920 |
| Iso-Pentane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 25.820 |
| 2-Methyl pentane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 130.180 |
| Cis-2-Hexene | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 6.790 |
| Methylcyclopentane | 0.000 | 0.000 | 0.001 | 0.306 | 0.000 | 0.000 | 0.306 | 13.490 |
| Benzene | 0.000 | 0.000 | 279.928 | 282.675 | 0.000 | 0.000 | 282.674 | 299.970 |
| Toluene | 0.000 | 0.000 | 0.071 | 85.825 | 0.000 | 0.000 | 85.820 | 85.820 |
| *o*-Xylene | 0.000 | 0.000 | 0.000 | 3.909 | 0.000 | 0.000 | 3.290 | 3.290 |
| Sulfolane | 0.000 | 0.000 | 0.000 | 1275.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| water | 110.000 | 250.000 | 0.000 | 0.000 | 5020.000 | 5020.000 | 0.003 | 0.000 |
| Total Flow kmol/hr | 254.414 | 578.214 | 149.350 | 633.353 | 11610.540 | 11610.540 | 191.040 | 331.718 |
| Total Flow tonne/day | 110.000 | 250.000 | 280.000 | 1647.714 | 5020.000 | 5020.000 | 372.093 | 650.000 |
| Total Flow cum/hr | 4.717 | 10.722 | 13.560 | 66.770 | 210.737 | 215.665 | 18.128 | 36.911 |
| Temperature C | 47.372 | 47.548 | 38.300 | 148.435 | 26.000 | 49.198 | 40.000 | 60.000 |
| Pressure kg/sqcm | 1.033 | 1.033 | 1.508 | 1.900 | 1.033 | 1.033 | 1.033 | 7.138 |
| Vapor Frac | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Liquid Frac | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Enthalpy kcal/kg | -3806.306 | -3806.103 | 155.936 | -604.141 | -3830.959 | -3804.201 | 126.501 | -130.062 |
| Enthalpy Btu/hr | -6.923E+07 | -1.573E+08 | 7.219E+06 | -1.646E+08 | -3.180E+09 | -3.158E+09 | 7.783E+06 | -1.398E+07 |
| Entropy cal/gm-K | -2.186 | -2.186 | -0.753 | -0.906 | -2.266 | -2.180 | -0.768 | -1.111 |
| Density kg/cum | 971.676 | 971.502 | 860.384 | 1028.227 | 992.550 | 969.869 | 855.234 | 733.756 |
| Average MW | 18.015 | 18.015 | 78.117 | 108.399 | 18.015 | 18.015 | 81.156 | 81.646 |
| Liq Vol 60F cum/hr | 4.592 | 10.437 | 13.219 | 59.773 | 209.570 | 209.570 | 17.628 | 35.004 |

*(continued on next page)*

| Stream | L | NONARMTS | ON | RCLS | REFLUX | RFLX | SOLVENT | SRB |
|---|---|---|---|---|---|---|---|---|
| To | EDC | | | RECLH | EDC | SRC | EDC | SRCP |
| From | FLASH | SPLIT | CLAYTOWR | SRCP | SPLIT | SPLT | RECLH | SRC |
| State | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID | LIQUID |
| Mass Flow tonne/day | | | | | | | | |
| n-Pentane | 17.400 | 29.719 | 0.000 | 0.000 | 143.524 | 0.000 | 0.000 | 0.000 |
| n-Hexane | 42.368 | 54.918 | 0.000 | 0.000 | 265.216 | 0.000 | 0.000 | 0.000 |
| Iso-Pentane | 14.410 | 25.819 | 0.000 | 0.000 | 124.686 | 0.000 | 0.000 | 0.000 |
| 2-Methyl pentane | 96.665 | 130.176 | 0.000 | 0.000 | 628.656 | 0.000 | 0.000 | 0.000 |
| Cis-2-Hexene | 5.366 | 6.789 | 0.000 | 0.000 | 32.783 | 0.000 | 0.000 | 0.000 |
| Methylcyclopentane | 10.991 | 13.188 | 0.305 | 0.000 | 63.696 | 0.066 | 0.000 | 0.000 |
| Benzene | 251.714 | 17.300 | 2.674 | 0.000 | 83.552 | 60.775 | 0.000 | 0.000 |
| Toluene | 79.961 | 0.000 | 0.000 | 0.005 | 0.000 | 18.451 | 0.005 | 0.005 |
| *o*-Xylene | 3.202 | 0.000 | 0.000 | 0.619 | 0.000 | 0.707 | 0.619 | 0.619 |
| Sulfolane | 0.000 | 0.000 | 0.000 | 1275.000 | 0.000 | 0.000 | 1275.000 | 1275.000 |
| water | 0.000 | 0.000 | 0.003 | 0.000 | 0.000 | 0.001 | 0.000 | 0.000 |
| Total Flow kmol/hr | 265.374 | 140.685 | 1.584 | 442.320 | 679.412 | 41.073 | 442.320 | 442.320 |
| Total Flow tonne/day | 522.078 | 277.909 | 2.983 | 1275.624 | 1342.113 | 80.000 | 1275.624 | 1275.624 |
| Total Flow cum/hr | 30.599 | 18.531 | 0.147 | 50.999 | 89.492 | 3.898 | 42.625 | 50.996 |
| Temperature C | 91.229 | 63.596 | 40.000 | 265.254 | 63.596 | 40.000 | 40.000 | 265.199 |
| Pressure kg/sqcm | 2.000 | 2.000 | 1.033 | 2.000 | 2.000 | 1.033 | 2.000 | 0.630 |
| Vapor Frac | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Liquid Frac | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Enthalpy kcal/kg | -86.682 | -485.413 | 97.906 | -778.804 | -485.411 | 126.501 | -874.213 | -778.853 |
| Enthalpy Btu/hr | -7.483E+06 | -2.231E+07 | 4.828E+04 | -1.643E+08 | -1.077E+08 | 1.673E+06 | -1.844E+08 | -1.643E+08 |
| Entropy cal/gm-K | -1.027 | -1.634 | -0.830 | -0.887 | -1.634 | -0.768 | -1.113 | -0.887 |
| Density kg/cum | 710.920 | 624.877 | 844.163 | 1042.209 | 624.877 | 855.234 | 1246.949 | 1042.265 |
| Average MW | 81.972 | 82.309 | 78.452 | 120.165 | 82.309 | 81.156 | 120.165 | 120.165 |
| Liq Vol 60F cum/hr | 27.719 | 17.375 | 0.143 | 42.145 | 83.910 | 3.790 | 42.145 | 42.145 |

(*continued on next page*)

| Stream | SRT | TOLUENE | TOP | V | WTR | WTRO | XYLENE |
|---|---|---|---|---|---|---|---|
| To | SRCH | | EDCH | EDC | SRC | | |
| From | SRC | TH | EDC | FLASH | | DECANTER | XH |
| State | VAPOR | LIQUID | VAPOR | VAPOR | LIQUID | LIQUID | LIQUID |
| Mass Flow tonne/day | | | | | | | |
| n-Pentane | 0.000 | 0.000 | 173.244 | 12.320 | 0.000 | 0.000 | 0.000 |
| n-Hexane | 0.000 | 0.000 | 320.136 | 12.552 | 0.000 | 0.000 | 0.000 |
| Iso-Pentane | 0.000 | 0.000 | 150.506 | 11.410 | 0.000 | 0.000 | 0.000 |
| 2-Methyl pentane | 0.000 | 0.000 | 758.836 | 33.515 | 0.000 | 0.000 | 0.000 |
| Cis-2-Hexene | 0.000 | 0.000 | 39.573 | 1.424 | 0.000 | 0.000 | 0.000 |
| Methylcyclopentane | 0.372 | 0.000 | 76.880 | 2.499 | 0.000 | 0.000 | 0.000 |
| Benzene | 343.449 | 0.023 | 100.848 | 48.256 | 0.000 | 0.000 | 0.000 |
| Toluene | 104.271 | 85.748 | 0.000 | 5.859 | 0.000 | 0.000 | 0.001 |
| *o*-Xylene | 3.997 | 0.026 | 0.000 | 0.088 | 0.000 | 0.000 | 3.264 |
| Sulfolane | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| water | 10.001 | 0.000 | 0.000 | 0.000 | 10.000 | 9.997 | 0.000 |
| Total Flow kmol/hr | 255.235 | 38.798 | 820.097 | 66.344 | 23.129 | 23.122 | 1.281 |
| Total Flow tonne/day | 462.091 | 85.796 | 1620.022 | 127.922 | 10.000 | 9.997 | 3.265 |
| Total Flow cum/hr | 12987.540 | 4.233 | 16204.380 | 968.968 | 0.419 | 0.426 | 0.157 |
| Temperature C | 68.640 | 44.700 | 69.435 | 91.229 | 25.000 | 40.000 | 40.000 |
| Pressure kg/sqcm | 0.560 | 1.233 | 1.400 | 2.000 | 1.000 | 1.033 | 1.289 |
| Vapor Frac | 1.000 | 0.000 | 1.000 | 1.000 | 0.000 | 0.000 | 0.000 |
| Liquid Frac | 0.000 | 1.000 | 0.000 | 0.000 | 1.000 | 1.000 | 1.000 |
| Enthalpy kcal/kg | 160.319 | 39.010 | -402.527 | -147.290 | -3832.115 | -3773.637 | -49.139 |
| Enthalpy Btu/hr | 1.225E+07 | 5.534E+05 | -1.078E+08 | -3.115E+06 | -6.336E+06 | -6.238E+06 | -2.653E+04 |
| Entropy cal/gm-K | -0.443 | -0.860 | -1.390 | -1.005 | -2.270 | -2.112 | -0.997 |
| Density kg/cum | 1.482 | 844.448 | 4.166 | 5.501 | 993.515 | 978.933 | 868.175 |
| Average MW | 75.436 | 92.140 | 82.309 | 80.341 | 18.015 | 18.015 | 106.163 |
| Liq Vol 60F cum/hr | 21.836 | 4.109 | 101.285 | 7.285 | 0.417 | 0.417 | 0.154 |

Performance index calculation for complete aromatic recovery unit with pure sulfolane as solvent is given in Table 6.18.

Table 6.18 Performance index of pure sulfolane for extractive distillation aromatic recovery unit

| $x_a^e$ | $x_a^r$ | $x_n^e$ | $x_n^r$ | $S_c$ | $S_s$ | $PI$ |
|---|---|---|---|---|---|---|
| 0.9992 | 0.0656 | 0.0008 | 0.9344 | 15.2327 | 17924.5022 | **273038.3772** |

Performance index for complete aromatic recovery unit with extractive distillation is approximately 3 times better than that of with simple liquid-liquid extraction discussed in chapter 4.

## 6.4 Conclusions

Aromatic recovery unit with extractive distillation has been simulated with ASPEN PLUS 10.2 a sequential modular simulation package. RK-SOAVE property method is used for vapor-liquid and NRTL-2 property method is used for liquid-liquid calculations in extractive distillation column. Performance index for complete aromatic recovery unit with extractive distillation is approximately 3 times better than conventional aromatic unit with liquid-liquid extraction.

## References


[1] J. C. gentry, C. S. Kumar, H. M. Lee, Y. H. Lee, "Operational Experience with GT-BTX$^{sm}$ Aromatics Recovery Technology", *GTC Technology Corporation*, USA and *Lg-Caltex oil Corporation*, Korea.

[2] J. C. Gentry, C. S. Kumar, R. Wright-Wytcherley, "Extractive Distillation applied", *AIChE Spring Meeting* 7e, New Orleans, LA, 2003.

[3] K. MinSu, N. Sangyoup, C. Jungho, K. Hwayong, "Simulation of Aromatic recovery Process by Extractive Distillation", *Korean Journal of Chemical Engineering* **19** (2002) 1-5.

[4] ASPEN Plus, Release 10.2.1, *Aspen technology Inc.*, Cambridge, MA, USA, 2000.

[5] R. Krishna, R. Taylor, *Multicomponent mass transfer*, Table 14.2, 1993.

# Chapter 7

# SUGGESTIONS FOR FUTURE WORK

## 7.1 Parameter Estimation

### 7.1.1 Common parameter estimation

It has been observed that the binary interaction parameters are different for a common binary pair appearing in two different multicomponent systems. This means that these parameters are applicable to that particular system and conditions and can not be used for other systems. Therefore, to overcome this problem one has to go for simultaneous parameter estimation to estimate the common parameters that are applicable to other multicomponent systems at other conditions. For this the objective function can be defined as the summation of objective function of individual systems.

### 7.1.2 Estimation of UNIQUAC structural parameters

For binary interaction parameters estimation for UNIQUAC model, we have taken the structural parameters either from literature or calculated from Aspen Plus. For more accurate predictions one could use these parameters calculated using polarizable continuum model [1].

### 7.1.3. Prediction of other properties

Binary interaction parameters of activity coefficient models are important in predicting liquid-liquid equilibrium, vapor liquid equilibrium, heat of mixing, and activity coefficient at infinite dilution. The present thesis was based only on the parameters for liquid-liquid equilibrium data. However the work can be extended for estimation of interaction parameters that are also applicable for prediction of vapor-liquid equilibrium, heat of mixing and activity coefficient at infinite dilution.

## 7.2 Simulation of aromatic recovery flowsheet

### 7.2.1 Tuning

Tuning in the present work was taken up with the use of parameters like boilup ratio, reflux ratio, split ratio, condenser and reboiler duty etc. These are all macro tunings. This exercise can bring down the gap between the plant data and aspen plus simulation results to certain extent. But after this stage it is very difficult to reduce the gap further. Micro tuning using user defined binary interaction parameters can be studied from this stage to further reduce the gap. That is, binary interaction parameters obtained by simultaneous parameter estimation (as suggested in section 7.1.1) should be used as user-defined input instead of the default values existing in aspen plus databank.

### 7.2.2 Simulation with other solvents

The present simulation of aromatic recovery process is carried out with pure sulfolane and mixed solvents upto 10 percent co-solvent in sulfolane. The same simulation programme can be extended to other pure solvents and mixed solvents covering 0-100 percent co-solvent in sulfolane. We can also search for mixed solvents involving other pairs better than sulfolane.

### 7.2.3 Optimization

The present simulation flowsheet can be used for optimization. Optimization module needs to be acquired for aspen plus. The objective function can be formulated for total heat requirement with product purities as constraints.

### 7.2.4 Energy integration

The major part of the utility requirement is in the fractionation section. The benzene and toluene column of fractionation section can be put to heat integration studies for reducing the utility costs. Adjusting the pressure and splitting the column in two parts can reduce the utility requirements in condensers and reboilers. Heat exchanger network analysis can also save a significant part of utility requirement in heat exchangers, reboilers and condensers.

## Reference

[1] T. Banerjee, M. K. Singh, R. K. Sahoo, A. Khanna, "Volume, surface, UNIQUAC interaction parameters for imidazolium based ionic liquids via Polarizable Continuum Model", *Fluid Phase Equilibria* **234** (2005) 64.

# Appendix A

Table A.1 GA Selection function and Operators [13,14]

| Functions/Operators | Type | Relationship | Notations |
|---|---|---|---|
| Selection Function | Normalized geometric ranking | $P_i = q'(1-q)^{r-1}; q' = \frac{q}{1-(1-q)^P}$ | $P_i$ = probability of selecting the $i$th individual, $q$ = probability of selecting the best individual, $r$ = rank of the individual, where 1 in the best, $P$ = population size |
| Genetic Operators | | $a_i$ and $b_i$ = lower and upper bound, respectively, for each variable $i$ | |
| | | $\bar{X}$ and $\bar{Y}$ = two $m$-dimensional row vectors denoting individuals (parents) from the population | |
| Mutation | Uniform | $x_i' = \begin{cases} U(a_i, b_i), & \text{if } i = j \\ x_i, & \text{otherwise} \end{cases}$ | |
| | Boundary | $x_i' = \begin{cases} a_i, \text{ if } i = j, r < 0.5 \\ b_i, \text{ if } i = j, r \geq 0.5 \\ x_i, \text{ otherwise} \end{cases}$ | $r = U(0,1)$ |
| | Non-uniform | $x_i' = \begin{cases} x_i + (b_i - x_i) f(G) \text{ if } r_1 < 0.5, \\ x_i - (x_i + a_i) f(G) \text{ if } r_1 \geq 0.5, \\ x_i, \quad \text{otherwise} \end{cases}$ where $f(G) = (r_2(1 - \frac{G}{G_{max}}))^b$ | $r_1, r_2 = U(0,1)$, $G$ = current generation, $b$ = shape parameter, $G_{max}$ = maximum number of generations |
| | Multi-non-uniform | Applies the non-uniform operator to all of the variables in the parent $\bar{X}$. | |
| Crossover | Simple | $x_i' = \begin{cases} x_i, & \text{if } i < r, \\ y_i, & \text{otherwise} \end{cases}; y_i' = \begin{cases} y_i, & \text{if } i < r, \\ x_i, & \text{otherwise} \end{cases}$ | $r = U(1, m)$ |
| | Arithmetic | $\bar{X}' = r\bar{X} + (1-r)\bar{Y}; \bar{Y}' = (1-r)\bar{X} + r\bar{Y}$ | $r = U(0,1)$ |
| | Heuristic | $\bar{X}' = \bar{X} + r(\bar{X} - \bar{Y}); \bar{Y}' = \bar{X}$ $feasibility = \begin{cases} 1, \text{ if } x_i' \geq a_i, x_i' \leq b_i \ \forall i \\ 0, \text{ otherwise} \end{cases}$ | $r = U(0,1)$ |

Table A.2 NRTL and UNIQUAC parameters for ternary hydrogen bonding systems

| System No. | $\alpha$ | $r$ | | | $q$ | | | Reference |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 1 | 2 | 3 | |
| 1 | 0.30 | 0.92 | 1.43 | 3.91 | 1.40 | 0.96 | 3.91 | [46] |
| 2 | 0.30 | 0.92 | 1.97 | 3.91 | 1.40 | 0.92 | 3.91 | [46] |
| 3 | 0.30 | 0.92 | 2.51 | 3.91 | 1.40 | 0.89 | 3.91 | [46] |
| 4 | 0.30 | 0.92 | 1.43 | 2.80 | 1.40 | 0.96 | 2.80 | [46] |
| 5 | 0.30 | 0.92 | 1.97 | 2.80 | 1.40 | 0.92 | 2.80 | [46] |
| 6 | 0.30 | 0.92 | 2.51 | 2.80 | 1.40 | 0.89 | 2.80 | [46] |
| 7 | 0.30 | 0.92 | 1.43 | 3.01 | 1.40 | 0.96 | 3.01 | [46] |
| 8 | 0.30 | 0.92 | 1.97 | 3.01 | 1.40 | 0.92 | 3.01 | [46] |
| 9 | 0.30 | 0.92 | 2.51 | 3.01 | 1.40 | 0.89 | 3.01 | [46] |
| 10 | 0.30 | 3.17 | 3.81 | 4.50 | 2.48 | 2.84 | 3.86 | [47] |
| 11 | 0.30 | 3.17 | 4.44 | 4.50 | 2.48 | 3.29 | 3.86 | [47] |
| 12 | 0.30 | 3.17 | 4.44 | 4.50 | 2.48 | 3.29 | 3.86 | [47] |
| 13 | 0.30 | 3.17 | 5.06 | 4.50 | 2.48 | 3.73 | 3.86 | [47] |
| 14 | 0.30 | 3.17 | 3.81 | 8.55 | 2.48 | 2.84 | 7.10 | [47] |
| 15 | 0.30 | 3.17 | 3.81 | 11.24 | 2.48 | 2.84 | 8.26 | [47] |
| 16 | 0.30 | 3.17 | 4.44 | 11.24 | 2.48 | 3.29 | 8.26 | [47] |
| 17 | 0.30 | 3.17 | 4.44 | 11.24 | 2.48 | 3.29 | 8.26 | [47] |
| 18 | 0.30 | 3.17 | 5.06 | 11.24 | 2.48 | 3.73 | 8.26 | [47] |
| 19 | 0.45 | 3.84 | 3.19 | 4.50 | 3.27 | 2.40 | 3.86 | [48] |
| 20 | 0.45 | 3.84 | 3.92 | 4.50 | 3.27 | 2.98 | 3.86 | [48] |
| 21 | 0.45 | 3.84 | 4.66 | 4.50 | 3.27 | 3.54 | 3.86 | [48] |
| 22 | 0.45 | 3.84 | 3.19 | 8.55 | 3.27 | 2.40 | 7.10 | [48] |
| 23 | 0.45 | 3.84 | 3.92 | 8.55 | 3.27 | 2.98 | 7.10 | [48] |
| 24 | 0.45 | 3.84 | 4.66 | 8.55 | 3.27 | 3.54 | 7.10 | [48] |
| 25 | 0.45 | 3.84 | 3.19 | 11.24 | 3.27 | 2.40 | 8.26 | [48] |
| 26 | 0.45 | 3.84 | 3.92 | 11.24 | 3.27 | 2.98 | 8.26 | [48] |
| 27 | 0.45 | 3.84 | 4.66 | 11.24 | 3.27 | 3.54 | 8.26 | [48] |
| 28 | 0.30 | 4.50 | 3.19 | 4.64 | 3.86 | 2.40 | 3.91 | [49] |
| 29 | 0.30 | 4.50 | 3.92 | 4.64 | 3.86 | 2.98 | 3.91 | [49] |
| 30 | 0.30 | 4.50 | 4.66 | 4.64 | 3.86 | 3.54 | 3.91 | [49] |
| 31 | 0.30 | 4.50 | 4.66 | 4.64 | 3.86 | 3.54 | 3.91 | [49] |
| 32 | 0.30 | 4.50 | 4.66 | 4.64 | 3.86 | 3.54 | 3.91 | [49] |
| 33 | 0.30 | 4.50 | 5.39 | 4.64 | 3.86 | 4.10 | 3.91 | [49] |
| 34 | 0.30 | 4.50 | 4.60 | 4.64 | 3.86 | 3.52 | 3.91 | [49] |
| 35 | 0.30 | 6.52 | 3.19 | 4.64 | 5.48 | 2.40 | 3.91 | [49] |
| 36 | 0.30 | 8.55 | 3.19 | 4.64 | 7.10 | 2.40 | 3.91 | [49] |
| 37 | 0.30 | 11.24 | 3.19 | 4.64 | 9.26 | 2.40 | 3.91 | [49] |
| 38 | 0.43 | 11.2432 | 3.1879 | 2.6908 | 9.256 | 2.400 | 1.904 | [50] |
| 39 | 0.43 | 11.2432 | 3.9229 | 2.6908 | 9.256 | 3.816 | 1.904 | [50] |
| 40 | 0.43 | 11.2432 | 3.3395 | 2.6908 | 9.256 | 3.536 | 1.904 | [50] |
| 41 | 0.43 | 11.2432 | 3.3395 | 2.6908 | 9.256 | 3.536 | 1.904 | [50] |

*(continued on next page)*

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 42 | 0.43 | 11.2432 | 3.3395 | 2.6908 | 9.256 | 3.536 | 1.904 | [50] |
| 43 | 0.35 | 11.2432 | 5.3929 | 2.6908 | 9.256 | 4.104 | 1.904 | [50] |
| 44 | 0.35 | 11.2432 | 4.5972 | 2.6908 | 9.256 | 3.508 | 1.904 | [50] |
| 45 | 0.35 | 9.8945 | 3.1879 | 2.6908 | 8.176 | 2.400 | 1.904 | [50] |
| 46 | 0.35 | 9.8945 | 3.9229 | 2.6908 | 8.176 | 3.816 | 1.904 | [50] |
| 47 | 0.35 | 9.8945 | 5.3929 | 2.6908 | 8.176 | 4.104 | 1.904 | [50] |
| 48 | 0.35 | 9.8945 | 4.5972 | 2.6908 | 8.176 | 3.508 | 1.904 | [50] |
| 49 | 0.30 | 4.06790 | 2.10547 | 0.92000 | 3.632 | 1.972 | 1.400 | [51] |
| 50 | 0.30 | 4.06790 | 4.80300 | 0.92000 | 3.632 | 4.132 | 1.400 | [51] |
| 51 | 0.20 | 2.8306 | 0.9200 | 1.4311 | 2.272 | 1.400 | 1.432 | [52] |
| 52 | 0.30 | 2.8108 | 0.9200 | 1.4311 | 2.440 | 1.400 | 1.432 | [52] |
| 53 | 0.30 | 1.4311 | 2.9644 | 0.9200 | 1.432 | 2.716 | 1.400 | [53] |
| 54 | 0.20 | 8.5462 | 5.4983 | 3.9810 | 7.096 | 4.356 | 3.200 | [54] |
| 55 | 0.20 | 9.8950 | 5.4983 | 3.9810 | 8.176 | 4.356 | 3.200 | [54] |
| 56 | 0.20 | 11.9182 | 5.4983 | 3.9810 | 9.796 | 4.356 | 3.200 | [54] |
| 57 | 0.35 | 5.5825 | 0.9200 | 2.1055 | 5.228 | 1.400 | 1.972 | [55] |
| 58 | 0.20 | 2.5735 | 3.5857 | 1.4311 | 2.336 | 3.060 | 1.432 | [56] |
| 59 | 0.20 | 3.2479 | 3.5857 | 2.1055 | 2.876 | 3.060 | 1.972 | [56] |
| 60 | 0.20 | 3.2479 | 3.5857 | 2.7791 | 2.876 | 3.060 | 2.508 | [56] |
| 61 | 0.30 | 4.0678 | 2.5755 | 0.9200 | 3.632 | 2.588 | 1.400 | [57] |
| 62 | 0.30 | 4.0678 | 6.6219 | 0.9200 | 3.632 | 5.828 | 1.400 | [57] |
| 63 | 0.30 | 6.6219 | 2.5755 | 0.9200 | 5.828 | 2.588 | 1.400 | [57] |

Table A.3 NRTL and UNIQUAC parameters for quaternary hydrogen bonding systems

| System No. | $\alpha$ | $r$ | | | | $q$ | | | | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | |
| 64 | 0.30 | 6.6219 | 4.0678 | 0.9200 | 2.5755 | 5.828 | 3.632 | 1.400 | 2.588 | [57] |
| 65 | 0.30 | 6.6219 | 4.7422 | 0.9200 | 1.4310 | 5.828 | 4.712 | 1.400 | 1.432 | [58] |

For reference please see chapter 2

# Appendix B

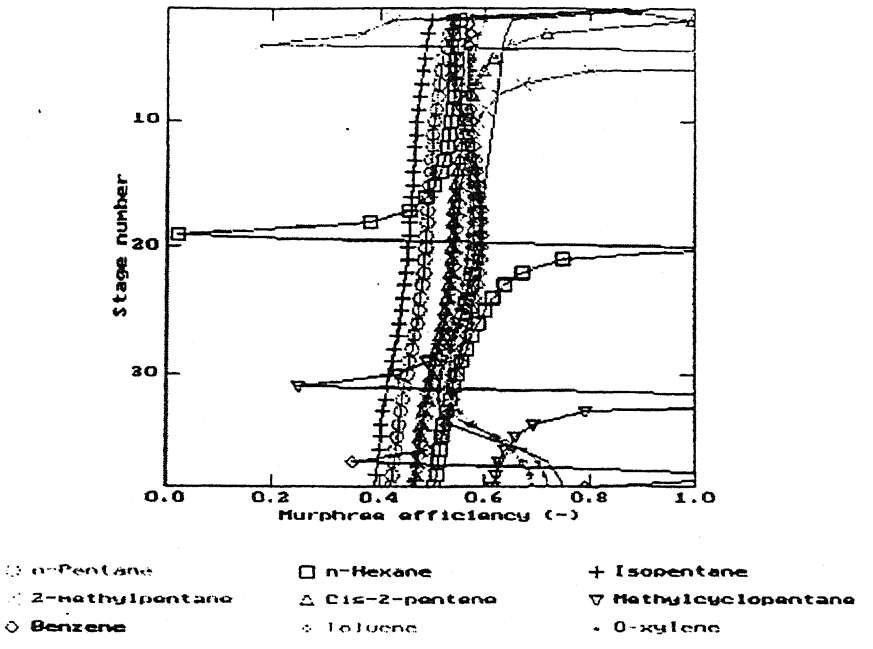



Figure B.1 Murphree efficiency plot for C203

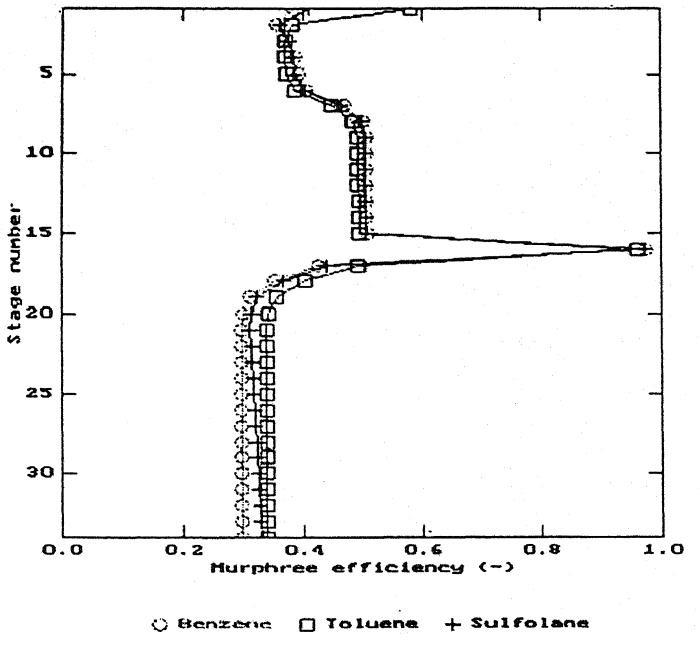



Figure B.2 Murphree efficiency plot for C204

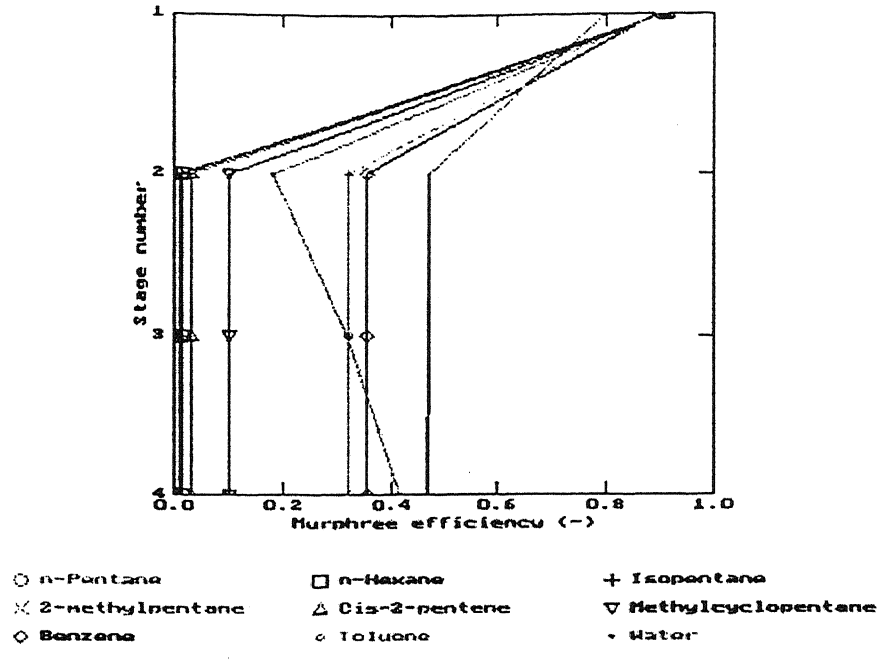



Figure B.3 Murphree efficiency plot for C205

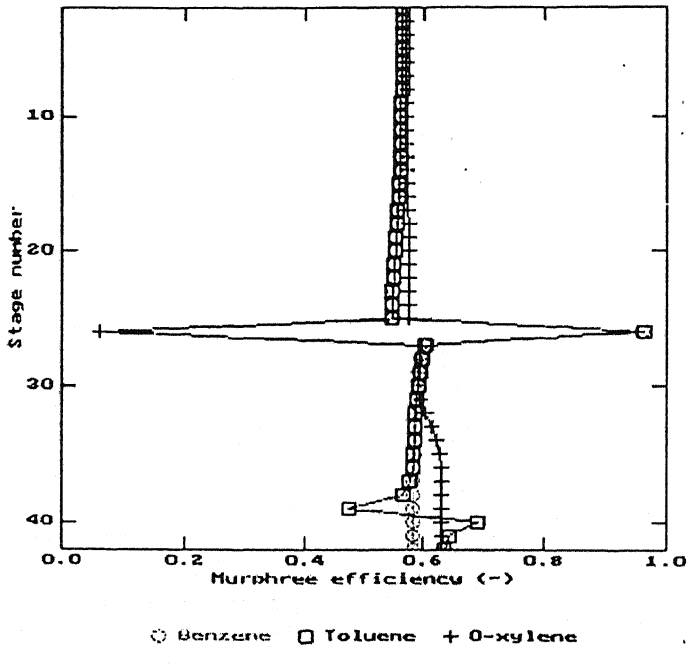



Figure B.4 Murphree efficiency plot for C207

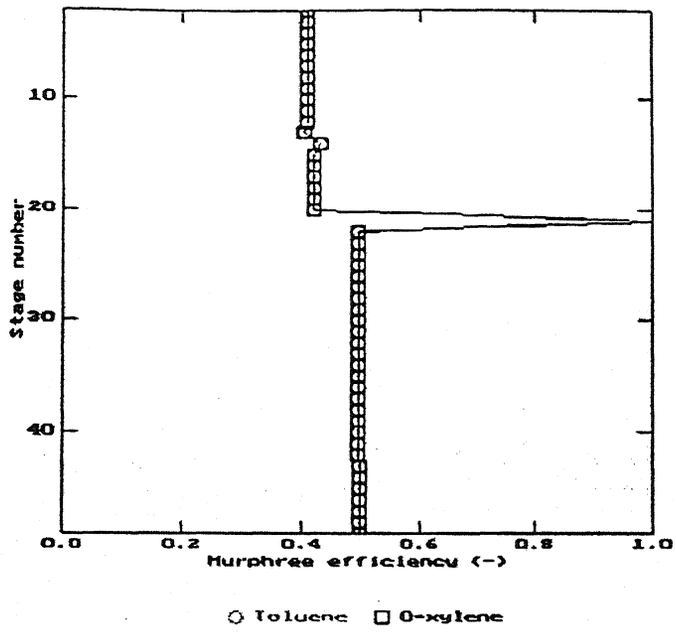



Figure B.5 Murphree efficiency plot for C208

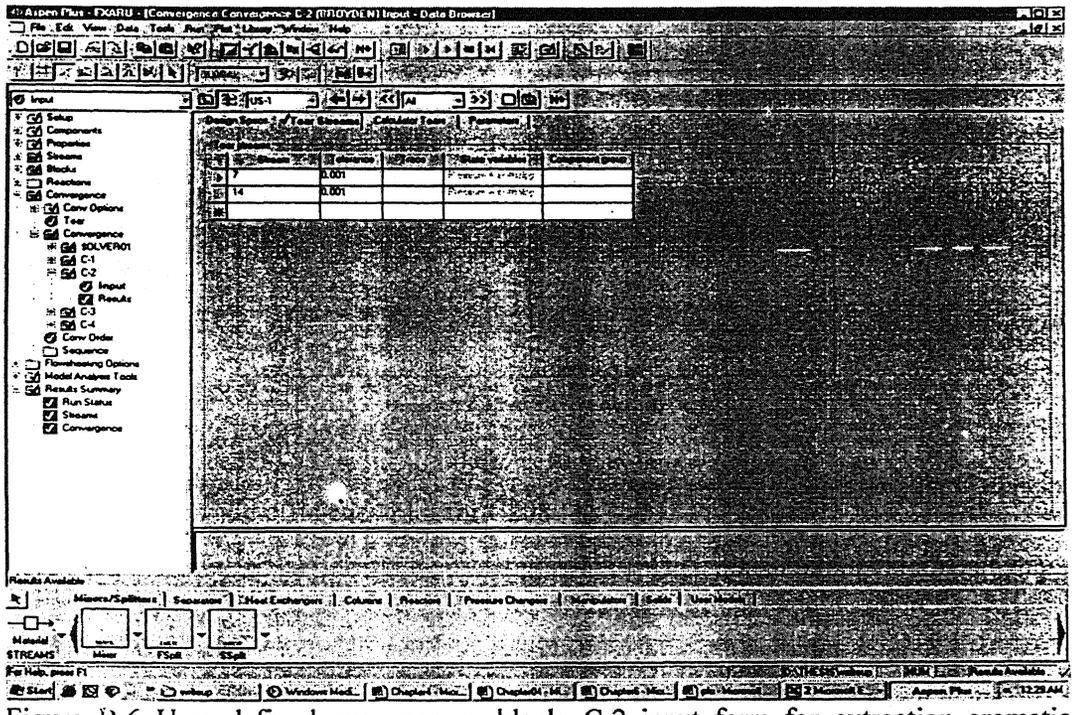


Figure B.6 User defined convergence block, C-2 input form for extraction aromatic recovery unit

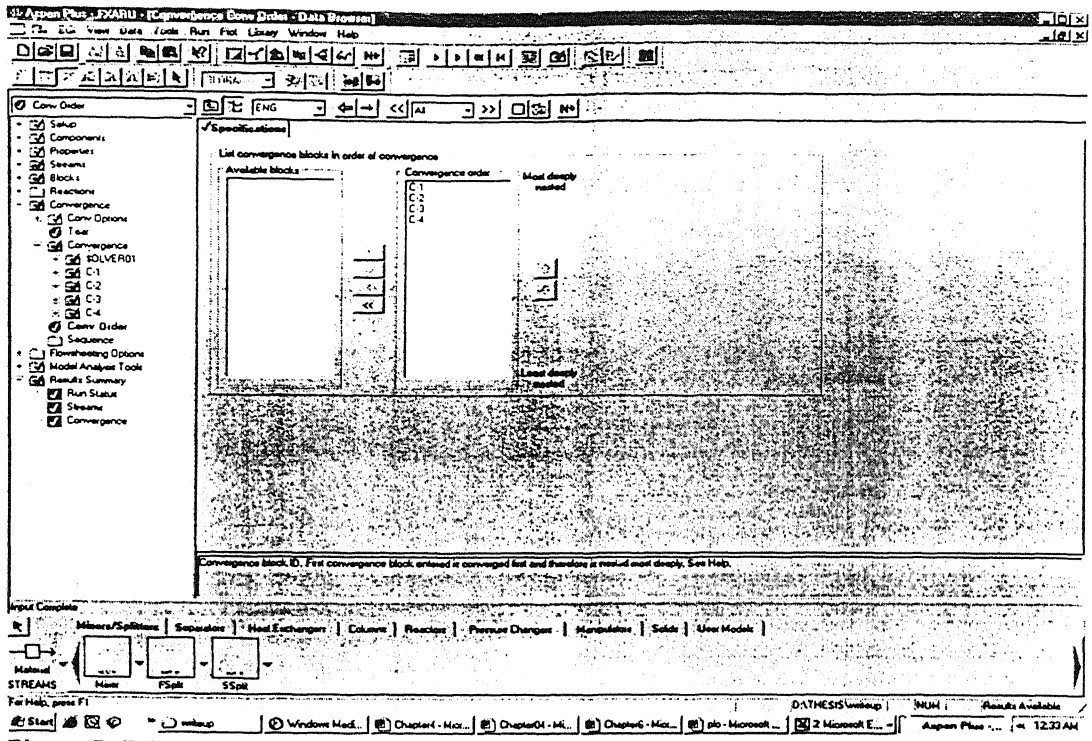


Figure B.7 Convergence order input form for extraction aromatic recovery unit

# Appendix C

Appendix C.1 ASPEN PLUS input summary for extractive distillation column

```
Input Summary created by Aspen Plus Rel. 10.2.1 at 02:53:47 Mon Aug 8, 2005

IN-UNITS MET MASS-FLOW='tonne/day' VOLUME-FLOW='cum/hr' &
    ENTHALPY-FLO='MMkcal/hr' HEAT-TRANS-C='kcal/hr-sqm-K' &
    PRESSURE='kg/sqcm' TEMPERATURE=C VOLUME=cum DELTA-T=C &
    HEAD=meter MOLE-DENSITY='kmol/cum' MASS-DENSITY='kg/cum' &
    MOLE-ENTHALP='kcal/mol' MASS-ENTHALP='kcal/kg' HEAT=MMkcal &
    MOLE-CONC='mol/l' PDROP-PER-HT='mbar/m' PDROP='kg/sqcm'

DEF-STREAMS CONVEN ALL

DESCRIPTION "
  General Simulation with English Units :
  F, psi, lb/hr, lbmol/hr, Btu/hr, cuft/hr.

  Property Method: None

  Flow basis for input: Mole

  Stream report composition: Mole flow "

DATABANKS PURE10 / AQUEOUS / SOLIDS / INORGANIC / &
    NOASPENPCD

PROP-SOURCES PURE10 / AQUEOUS / SOLIDS / INORGANIC
```

```
COMPONENTS
  N-PEN-01 C5H12-1 /
  N-HEX-01 C6H14-1 /
  2-MET-01 C5H12-2 /
  2-MET-02 C6H14-2 /
  CIS-2-01 C6H12-4 /
  METHY-01 C6H12-2 /
  BENZE-01 C6H6 /
  TOLUE-01 C7H8 /
  O-XYL-01 C8H10-1 /
  SULFO-01 C4H8O2S /
  WATER H2O

FLOWSHEET
  BLOCK FLASH IN=FEED OUT=V L
  BLOCK EDC IN=L V REFLUX SOLVENT OUT=TOP BOTTOM
  BLOCK PUMP IN=1 OUT=2
  BLOCK SPLIT IN=2 OUT=REFLUX NONARMTS
  BLOCK HEX IN=TOP CWI OUT=1 CWO

PROPERTIES RK-SOAVE
  PROPERTIES NRTL-2

PROP-DATA RKSKIJ-1
  IN-UNITS ENG
  PROP-LIST RKSKIJ
  BPVAL N-PEN-01 2-MET-01 0.0
  BPVAL N-PEN-01 BENZE-01 .0222000000
  BPVAL 2-MET-01 N-PEN-01 0.0
  BPVAL N-HEX-01 BENZE-01 .0141000000
  BPVAL BENZE-01 N-PEN-01 .0222000000
```

```
  BPVAL BENZE-01 N-HEX-01 .0141000000

PROP-DATA NRTL-2
  IN-UNITS MET MASS-FLOW='tonne/day' VOLUME-FLOW='cum/hr' &
    ENTHALPY-FLO='MMkcal/hr' HEAT-TRANS-C='kcal/hr-sqm-K' &
    PRESSURE='kg/sqcm' TEMPERATURE=C VOLUME=cum DELTA-T=C &
    HEAD=meter MOLE-DENSITY='kmol/cum' MASS-DENSITY='kg/cum' &
    MOLE-ENTHALP='kcal/mol' MASS-ENTHALP='kcal/kg' HEAT=MMkcal &
    MOLE-CONC='mol/l' PDROP-PER-HT='mbar/m' PDROP='kg/sqcm'
  PROP-LIST NRTL 2
  BPVAL N-PEN-01 N-HEX-01 0.0 188.9527000 .3000000000 0.0 &
    0.0 0.0 25.00000000 68.20000000
  BPVAL N-HEX-01 N-PEN-01 0.0 -180.4249000 .3000000000 0.0 &
    0.0 0.0 25.00000000 68.20000000
  BPVAL N-PEN-01 METHY-01 0.0 98.90430000 .3000000000 0.0 &
    0.0 0.0 36.05000000 71.80000000
  BPVAL METHY-01 N-PEN-01 0.0 -73.47240000 .3000000000 0.0 &
    0.0 0.0 36.05000000 71.80000000
  BPVAL N-PEN-01 BENZE-01 0.0 2.125100000 .3000000000 0.0 &
    0.0 0.0 35.00000000 40.00000000
  BPVAL BENZE-01 N-PEN-01 0.0 199.0059000 .3000000000 0.0 &
    0.0 0.0 35.00000000 40.00000000
  BPVAL N-PEN-01 TOLUE-01 0.0 592.6941000 .3000000000 0.0 &
    0.0 0.0 36.03000000 110.5600000
  BPVAL TOLUE-01 N-PEN-01 0.0 -222.3469000 .3000000000 0.0 &
    0.0 0.0 36.03000000 110.5600000
  BPVAL N-PEN-01 WATER -10.68920000 5051.727500 .2000000000 &
    0.0 0.0 0.0 0.0 30.00000000
  BPVAL WATER N-PEN-01 12.38660000 -791.7913000 .2000000000 &
    0.0 0.0 0.0 0.0 30.00000000
  BPVAL N-HEX-01 2-MET-01 0.0 -57.69500000 .3000000000 0.0 &
```

0.0 0.0 27.77000000 68.60000000

BPVAL 2-MET-01 N-HEX-01 0.0 52.83600000 .3000000000 0.0 &

0.0 0.0 27.77000000 68.60000000

BPVAL N-HEX-01 2-MET-02 0.0 -199.6220000 .3000000000 0.0 &

0.0 0.0 10.00000000 40.00000000

BPVAL 2-MET-02 N-HEX-01 0.0 261.1496000 .3000000000 0.0 &

0.0 0.0 10.00000000 40.00000000

BPVAL N-HEX-01 METHY-01 0.0 -153.9573000 .3000000000 0.0 &

0.0 0.0 31.68000000 71.85000000

BPVAL METHY-01 N-HEX-01 0.0 190.1605000 .3000000000 0.0 &

0.0 0.0 31.68000000 71.85000000

BPVAL N-HEX-01 BENZE-01 .4066000000 -213.7349000 .3000000000 &

0.0 0.0 0.0 25.00000000 79.60000000

BPVAL BENZE-01 N-HEX-01 -1.554000000 797.5720000 .3000000000 &

0.0 0.0 0.0 25.00000000 79.60000000

BPVAL N-HEX-01 TOLUE-01 1.518200000 -595.6702000 .3000000000 &

0.0 0.0 0.0 24.80000000 110.6500000

BPVAL TOLUE-01 N-HEX-01 -2.948300000 1259.245800 .3000000000 &

0.0 0.0 0.0 24.80000000 110.6500000

BPVAL N-HEX-01 WATER -9.827300000 4815.058600 .2000000000 &

0.0 0.0 0.0 0.0 55.00000000

BPVAL WATER N-HEX-01 7.649700000 962.7409000 .2000000000 &

0.0 0.0 0.0 0.0 55.00000000

BPVAL 2-MET-01 TOLUE-01 -16.13200000 5828.759300 .3000000000 &

0.0 0.0 0.0 27.90000000 110.7000000

BPVAL TOLUE-01 2-MET-01 9.727800000 -3434.109100 .3000000000 &

0.0 0.0 0.0 27.90000000 110.7000000

BPVAL 2-MET-01 WATER -7.640300000 4148.017100 .2000000000 &

0.0 0.0 0.0 0.0 25.00000000

BPVAL WATER 2-MET-01 12.67300000 -934.1636000 .2000000000 &

0.0 0.0 0.0 0.0 25.00000000

```
BPVAL 2-MET-02 BENZE-01 0.0 -3.466500000 .3000000000 0.0 &
  0.0 0.0 10.00000000 50.00000000
BPVAL BENZE-01 2-MET-02 0.0 239.1201000 .3000000000 0.0 &
  0.0 0.0 10.00000000 50.00000000
BPVAL 2-MET-02 WATER -5.412000000 3565.592300 .2000000000 &
  0.0 0.0 0.0 0.0 25.00000000
BPVAL WATER 2-MET-02 12.88480000 -577.0172000 .2000000000 &
  0.0 0.0 0.0 0.0 25.00000000
BPVAL METHY-01 BENZE-01 0.0 -7.786200000 .3000000000 0.0 &
  0.0 0.0 55.00000000 80.15000000
BPVAL BENZE-01 METHY-01 0.0 151.2524000 .3000000000 0.0 &
  0.0 0.0 55.00000000 80.15000000
BPVAL METHY-01 TOLUE-01 0.0 345.8701000 .3000000000 0.0 &
  0.0 0.0 71.80000000 110.6500000
BPVAL TOLUE-01 METHY-01 0.0 -186.4291000 .3000000000 0.0 &
  0.0 0.0 71.80000000 110.6500000
BPVAL METHY-01 WATER -8.947000000 4405.205600 .2000000000 &
  0.0 0.0 0.0 10.00000000 30.00000000
BPVAL WATER METHY-01 8.807000000 296.7077000 .2000000000 &
  0.0 0.0 0.0 10.00000000 30.00000000
BPVAL BENZE-01 TOLUE-01 -2.885200000 1123.950100 .3000000000 &
  0.0 0.0 0.0 40.00000000 110.7500000
BPVAL TOLUE-01 BENZE-01 2.191100000 -863.7308000 .3000000000 &
  0.0 0.0 0.0 40.00000000 110.7500000
BPVAL BENZE-01 SULFO-01 0.0 498.8326000 .3000000000 0.0 &
  0.0 0.0 30.00000000 139.5000000
BPVAL SULFO-01 BENZE-01 0.0 -50.44760000 .3000000000 0.0 &
  0.0 0.0 30.00000000 139.5000000
BPVAL BENZE-01 WATER 45.19050000 591.3676000 .2000000000 &
  0.0 -7.562900000 0.0 .8000000000 77.00000000
BPVAL WATER BENZE-01 140.0874000 -5954.307100 .2000000000 &
```

```
    0.0 -20.02540000 0.0 .8000000000 77.00000000
  BPVAL TOLUE-01 SULFO-01 1.398400000 71.40790000 .3000000000 &
    0.0 0.0 0.0 30.00000000 166.0000000
  BPVAL SULFO-01 TOLUE-01 -.3310000000 223.1410000 .3000000000 &
    0.0 0.0 0.0 30.00000000 166.0000000
  BPVAL TOLUE-01 WATER -247.8792000 14759.75980 .2000000000 &
    0.0 35.58200000 0.0 -9.000000000 93.00000000
  BPVAL WATER TOLUE-01 627.0528000 -27269.35550 .2000000000 &
    0.0 -92.71820000 0.0 -9.000000000 93.00000000
  BPVAL O-XYL-01 WATER -5.627500000 2996.678700 .2000000000 &
    0.0 0.0 0.0 0.0 25.00000000
  BPVAL WATER O-XYL-01 4.238800000 1246.887600 .2000000000 &
    0.0 0.0 0.0 0.0 25.00000000
  BPVAL O-XYL-01 SULFO-01 0.0 692.5672000 .3000000000 0.0 &
    0.0 0.0 60.00000000 60.00000000
  BPVAL SULFO-01 O-XYL-01 0.0 94.18210000 .3000000000 0.0 &
    0.0 0.0 60.00000000 60.00000000
  BPVAL SULFO-01 WATER 0.0 333.4163000 .6000000000 0.0 0.0 &
    0.0 15.00000000 50.00000000
  BPVAL WATER SULFO-01 0.0 432.7332000 .6000000000 0.0 0.0 &
    0.0 15.00000000 50.00000000

PROP-SET VLLE
  IN-UNITS ENG
  PROPNAME-LIS PHIMX GAMMA PL SUBSTREAM=MIXED PHASE=V L1 L2
; "Fugacity, activity, and vapor pressure"


STREAM CWI
  SUBSTREAM MIXED TEMP=26. PRES=1. <atm> MASS-FLOW=5020.
  MASS-FRAC WATER 1.
```

```
STREAM FEED
  IN-UNITS ENG
  SUBSTREAM MIXED TEMP=60. <C> PRES=7. <bar>
  MASS-FLOW N-PEN-01 29.72 <tonne/day> / N-HEX-01  &
    54.92 <tonne/day> / 2-MET-01 25.82 <tonne/day> /  &
    2-MET-02 130.18 <tonne/day> / CIS-2-01 6.79 <tonne/day>  &
    / METHY-01 13.49 <tonne/day> / BENZE-01  &
    299.97 <tonne/day> / TOLUE-01 85.82 <tonne/day> /  &
    O-XYL-01 3.29 <tonne/day>

STREAM REFLUX
  SUBSTREAM MIXED TEMP=55.1789128 PRES=1.96133
  MASS-FLOW N-PEN-01 143.228916 / N-HEX-01 264.674696 /  &
    2-MET-01 124.433735 / 2-MET-02 627.373494 / CIS-2-01  &
    32.7227966 / METHY-01 28.4267209 / BENZE-01 0.67173207  &
    / TOLUE-01 3.8681E-007 / O-XYL-01 1.226E-012 /  &
    SULFO-01 1.2466E-008 / WATER 0.

STREAM SOLVENT
  IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='MMkcal/hr'  &
    HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE='kg/sqcm'  &
    TEMPERATURE=C VOLUME=cum DELTA-T=C HEAD=meter  &
    MOLE-ENTHALP='kcal/mol' MASS-ENTHALP='kcal/kg' HEAT=MMkcal  &
    MOLE-CONC='mol/l' PDROP-PER-HT='mbar/m' PDROP='kg/sqcm'
  SUBSTREAM MIXED TEMP=40. PRES=2.
  MASS-FLOW SULFO-01 1275. <tonne/day>

BLOCK SPLIT FSPLIT
  FRAC REFLUX 0.82815735
```

```
BLOCK FLASH FLASH2
  IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='MMkcal/hr' &
    HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE='kg/sqcm' &
    TEMPERATURE=C VOLUME=cum DELTA-T=C HEAD=meter &
    MOLE-ENTHALP='kcal/mol' MASS-ENTHALP='kcal/kg' HEAT=MMkcal &
    MOLE-CONC='mol/l' PDROP-PER-HT='mbar/m' PDROP='kg/sqcm'
  PARAM PRES=2. VFRAC=0.2

BLOCK HEX HEATX
  PARAM VFRAC-HOT=0.
  FEEDS HOT=TOP COLD=CWI
  PRODUCTS HOT=1 COLD=CWO

BLOCK EDC RADFRAC
  IN-UNITS MET VOLUME-FLOW='cum/hr' ENTHALPY-FLO='MMkcal/hr' &
    HEAT-TRANS-C='kcal/hr-sqm-K' PRESSURE='kg/sqcm' &
    TEMPERATURE=C VOLUME=cum DELTA-T=C HEAD=meter &
    MOLE-ENTHALP='kcal/mol' MASS-ENTHALP='kcal/kg' HEAT=MMkcal &
    MOLE-CONC='mol/l' PDROP-PER-HT='mbar/m' PDROP='kg/sqcm'
  PARAM NSTAGE=60 EFF=MURPHREE ABSORBER=NO NPHASE=3
  COL-CONFIG CONDENSER=PARTIAL-V REBOILER=THERMOSYPHON
  PROP-SECTION 1 60 RK-SOAVE PHASE-EQM=VL1 / 4 19 NRTL-2 &
    PHASE-EQM=LL
  FEEDS L 20 / V 33 / REFLUX 2 / SOLVENT 4
  PRODUCTS TOP 1 V / BOTTOM 60 L
  P-SPEC 1 1.4
  COL-SPECS QN=20. DP-COL=0.5 MASS-D=1600. <tonne/day>
  THERMOSYPHON PRES=1.9 TEMP=162.
  COMP-EFF 1 N-PEN-01 1. / 1 N-HEX-01 1. / 1 2-MET-01 &
    1. / 1 2-MET-02 1. / 1 CIS-2-01 1. / 1 METHY-01 &
    1. / 1 BENZE-01 1. / 1 TOLUE-01 1. / 1 O-XYL-01 &
```

1. / 1 SULFO-01 1. / 2 N-PEN-01 0.6656 / 2 &
N-HEX-01 0.6588 / 2 2-MET-01 0.6474 / 2 2-MET-02 &
0.6589 / 2 CIS-2-01 0.6702 / 2 METHY-01 0.7588 / 2 &
BENZE-01 0.6337 / 2 TOLUE-01 0.7104 / 2 O-XYL-01 &
0.7096 / 2 SULFO-01 0.7149 / 3 N-PEN-01 0.6614 / 3 &
N-HEX-01 0.6526 / 3 2-MET-01 0.6437 / 3 2-MET-02 &
0.6584 / 3 CIS-2-01 0.6659 / 3 METHY-01 0.7134 / 3 &
BENZE-01 1. / 3 TOLUE-01 0.7134 / 3 O-XYL-01 0.7129 &
/ 3 SULFO-01 0.7183 / 4 N-PEN-01 0.655 / 4 &
N-HEX-01 0.6932 / 4 2-MET-01 0.6351 / 4 2-MET-02 &
0.6196 / 4 CIS-2-01 0.6659 / 4 METHY-01 0.7472 / 4 &
BENZE-01 0.7197 / 4 TOLUE-01 0.7254 / 4 O-XYL-01 &
0.7251 / 4 SULFO-01 0.8408 / 5 N-PEN-01 0.6535 / 5 &
N-HEX-01 0.6859 / 5 2-MET-01 0.6283 / 5 2-MET-02 &
0.5995 / 5 CIS-2-01 0.6649 / 5 METHY-01 0.6796 / 5 &
BENZE-01 0.7342 / 5 TOLUE-01 0.7477 / 5 O-XYL-01 &
0.7493 / 5 SULFO-01 0.6779 / 6 N-PEN-01 0.6515 / 6 &
N-HEX-01 0.6913 / 6 2-MET-01 0.6262 / 6 2-MET-02 &
0.4032 / 6 CIS-2-01 0.6626 / 6 METHY-01 0.682 / 6 &
BENZE-01 0.7364 / 6 TOLUE-01 0.7495 / 6 O-XYL-01 &
0.7513 / 6 SULFO-01 0.6591 / 7 N-PEN-01 0.6505 / 7 &
N-HEX-01 0.6959 / 7 2-MET-01 0.6257 / 7 2-MET-02 &
0.8246 / 7 CIS-2-01 0.6614 / 7 METHY-01 0.6897 / 7 &
BENZE-01 0.7373 / 7 TOLUE-01 0.7499 / 7 O-XYL-01 &
0.7517 / 7 SULFO-01 0.6586 / 8 N-PEN-01 0.6501 / 8 &
N-HEX-01 0.6987 / 8 2-MET-01 0.626 / 8 2-MET-02 &
0.7376 / 8 CIS-2-01 0.6609 / 8 METHY-01 0.6959 / 8 &
BENZE-01 0.7376 / 8 TOLUE-01 0.7501 / 8 O-XYL-01 &
0.7519 / 8 SULFO-01 0.6586 / 9 N-PEN-01 0.6503 / 9 &
N-HEX-01 0.7001 / 9 2-MET-01 0.6274 / 9 2-MET-02 &
0.7186 / 9 CIS-2-01 0.6609 / 9 METHY-01 0.6997 / 9 &

BENZE-01 0.7377 / 9 TOLUE-01 0.7501 / 9 O-XYL-01 &
0.7519 / 9 SULFO-01 0.6558 / 10 N-PEN-01 0.6513 / &
10 N-HEX-01 0.7004 / 10 2-MET-01 0.6307 / 10 &
2-MET-02 0.7115 / 10 CIS-2-01 0.6617 / 10 METHY-01 &
0.7016 / 10 BENZE-01 0.7376 / 10 TOLUE-01 0.75 / &
10 O-XYL-01 0.7519 / 10 SULFO-01 0.648 / 11 &
N-PEN-01 0.6537 / 11 N-HEX-01 0.7001 / 11 2-MET-01 &
0.6374 / 11 2-MET-02 0.7085 / 11 CIS-2-01 0.6635 / &
11 METHY-01 0.7019 / 11 BENZE-01 0.7374 / 11 &
TOLUE-01 0.7499 / 11 O-XYL-01 0.7518 / 11 SULFO-01 &
0.6328 / 12 N-PEN-01 0.6584 / 12 N-HEX-01 0.699 / &
12 2-MET-01 0.6498 / 12 2-MET-02 0.7071 / 12 &
CIS-2-01 0.6672 / 12 METHY-01 0.7009 / 12 BENZE-01 &
0.7371 / 12 TOLUE-01 0.7497 / 12 O-XYL-01 0.7516 / &
12 SULFO-01 0.6054 / 13 N-PEN-01 0.6667 / 13 &
N-HEX-01 0.6973 / 13 2-MET-01 0.6691 / 13 2-MET-02 &
0.7067 / 13 CIS-2-01 0.6738 / 13 METHY-01 0.6988 / &
13 BENZE-01 0.7367 / 13 TOLUE-01 0.7494 / 13 &
O-XYL-01 0.7514 / 13 SULFO-01 0.5536 / 14 N-PEN-01 &
0.6796 / 14 N-HEX-01 0.6946 / 14 2-MET-01 0.6932 / &
14 2-MET-02 0.7068 / 14 CIS-2-01 0.6845 / 14 &
METHY-01 0.6952 / 14 BENZE-01 0.7361 / 14 TOLUE-01 &
0.749 / 14 O-XYL-01 0.7511 / 14 SULFO-01 0.4373 / &
15 N-PEN-01 0.6966 / 15 N-HEX-01 0.6901 / 15 &
2-MET-01 0.7167 / 15 2-MET-02 0.7073 / 15 CIS-2-01 &
0.6999 / 15 METHY-01 0.6891 / 15 BENZE-01 0.7354 / &
15 TOLUE-01 0.7485 / 15 O-XYL-01 0.7506 / 15 &
SULFO-01 0.0242 / 16 N-PEN-01 0.7152 / 16 N-HEX-01 &
0.6823 / 16 2-MET-01 0.736 / 16 2-MET-02 0.7079 / &
16 CIS-2-01 0.7194 / 16 METHY-01 0.6784 / 16 &
BENZE-01 0.7343 / 16 TOLUE-01 0.7478 / 16 O-XYL-01 &

0.75 / 16 SULFO-01 1. / 17 N-PEN-01 0.7322 / 17 &
N-HEX-01 0.6661 / 17 2-MET-01 0.7508 / 17 2-MET-02 &
0.7086 / 17 CIS-2-01 0.7407 / 17 METHY-01 0.6558 / &
17 BENZE-01 0.7328 / 17 TOLUE-01 0.7467 / 17 &
O-XYL-01 0.7491 / 17 SULFO-01 1. / 18 N-PEN-01 &
0.7457 / 18 N-HEX-01 0.6136 / 18 2-MET-01 0.7622 / &
18 2-MET-02 0.7093 / 18 CIS-2-01 0.7603 / 18 &
METHY-01 0.5833 / 18 BENZE-01 0.7306 / 18 TOLUE-01 &
0.7453 / 18 O-XYL-01 0.7478 / 18 SULFO-01 1. / 19 &
N-PEN-01 0.949 / 19 N-HEX-01 0.7912 / 19 2-MET-01 &
0.977 / 19 2-MET-02 0.6821 / 19 CIS-2-01 0.96 / 19 &
METHY-01 0.4745 / 19 BENZE-01 0.6949 / 19 TOLUE-01 &
0.7103 / 19 O-XYL-01 0.7127 / 19 SULFO-01 0.8753 / &
20 N-PEN-01 0.6547 / 20 N-HEX-01 0.6975 / 20 &
2-MET-01 0.6278 / 20 2-MET-02 0.7346 / 20 CIS-2-01 &
0.6655 / 20 METHY-01 0.6897 / 20 BENZE-01 0.6926 / &
20 TOLUE-01 0.6775 / 20 O-XYL-01 0.6685 / 20 &
SULFO-01 0.6579 / 21 N-PEN-01 0.6536 / 21 N-HEX-01 &
0.7002 / 21 2-MET-01 0.627 / 21 2-MET-02 0.7183 / &
21 CIS-2-01 0.6642 / 21 METHY-01 0.6949 / 21 &
BENZE-01 0.6989 / 21 TOLUE-01 0.682 / 21 O-XYL-01 &
0.6724 / 21 SULFO-01 0.6587 / 22 N-PEN-01 0.6536 / &
22 N-HEX-01 0.7018 / 22 2-MET-01 0.6275 / 22 &
2-MET-02 0.7115 / 22 CIS-2-01 0.6638 / 22 METHY-01 &
0.6986 / 22 BENZE-01 0.7045 / 22 TOLUE-01 0.6866 / &
22 O-XYL-01 0.6767 / 22 SULFO-01 0.6603 / 23 &
N-PEN-01 0.6538 / 23 N-HEX-01 0.7022 / 23 2-MET-01 &
0.6284 / 23 2-MET-02 0.7078 / 23 CIS-2-01 0.6633 / &
23 METHY-01 0.7003 / 23 BENZE-01 0.7084 / 23 &
TOLUE-01 0.6893 / 23 O-XYL-01 0.679 / 23 SULFO-01 &
0.6602 / 24 N-PEN-01 0.6549 / 24 N-HEX-01 0.702 / &

24 2-MET-01 0.631 / 24 2-MET-02 0.7055 / 24 &
CIS-2-01 0.6632 / 24 METHY-01 0.7008 / 24 BENZE-01 &
0.7115 / 24 TOLUE-01 0.6908 / 24 O-XYL-01 0.68 / &
24 SULFO-01 0.6585 / 25 N-PEN-01 0.6571 / 25 &
N-HEX-01 0.7012 / 25 2-MET-01 0.6363 / 25 2-MET-02 &
0.7039 / 25 CIS-2-01 0.6635 / 25 METHY-01 0.7004 / &
25 BENZE-01 0.7143 / 25 TOLUE-01 0.6919 / 25 &
O-XYL-01 0.68 / 25 SULFO-01 0.655 / 26 N-PEN-01 &
0.6609 / 26 N-HEX-01 0.7002 / 26 2-MET-01 0.6456 / &
26 2-MET-02 0.7027 / 26 CIS-2-01 0.6644 / 26 &
METHY-01 0.6994 / 26 BENZE-01 0.7171 / 26 TOLUE-01 &
0.694 / 26 O-XYL-01 0.6799 / 26 SULFO-01 0.6493 / &
27 N-PEN-01 0.6668 / 27 N-HEX-01 0.6987 / 27 &
2-MET-01 0.6592 / 27 2-MET-02 0.7017 / 27 CIS-2-01 &
0.6661 / 27 METHY-01 0.6975 / 27 BENZE-01 0.72 / &
27 TOLUE-01 0.6986 / 27 O-XYL-01 0.6812 / 27 &
SULFO-01 0.6401 / 28 N-PEN-01 0.6749 / 28 N-HEX-01 &
0.6966 / 28 2-MET-01 0.6754 / 28 2-MET-02 0.7008 / &
28 CIS-2-01 0.6692 / 28 METHY-01 0.6946 / 28 &
BENZE-01 0.723 / 28 TOLUE-01 0.7077 / 28 O-XYL-01 &
0.6876 / 28 SULFO-01 0.6252 / 29 N-PEN-01 0.6846 / &
29 N-HEX-01 0.6936 / 29 2-MET-01 0.6909 / 29 &
2-MET-02 0.7 / 29 CIS-2-01 0.674 / 29 METHY-01 &
0.6898 / 29 BENZE-01 0.7257 / 29 TOLUE-01 0.7206 / &
29 O-XYL-01 0.704 / 29 SULFO-01 0.5982 / 30 &
N-PEN-01 0.6947 / 30 N-HEX-01 0.6889 / 30 2-MET-01 &
0.703 / 30 2-MET-02 0.6994 / 30 CIS-2-01 0.6811 / &
30 METHY-01 0.6811 / 30 BENZE-01 0.7279 / 30 &
TOLUE-01 0.7335 / 30 O-XYL-01 0.7269 / 30 SULFO-01 &
0.532 / 31 N-PEN-01 0.7038 / 31 N-HEX-01 0.6803 / &
31 2-MET-01 0.7101 / 31 2-MET-02 0.6988 / 31 &

CIS-2-01 0.6904 / 31 METHY-01 0.6619 / 31 BENZE-01 &
0.7292 / 31 TOLUE-01 0.7425 / 31 O-XYL-01 0.744 / &
31 SULFO-01 0.0001 / 32 N-PEN-01 0.995 / 32 &
N-HEX-01 0.8707 / 32 2-MET-01 0.9978 / 32 2-MET-02 &
0.6982 / 32 CIS-2-01 0.9908 / 32 METHY-01 0.8872 / &
32 BENZE-01 0.0001 / 32 TOLUE-01 0.0001 / 32 &
O-XYL-01 0.0001 / 32 SULFO-01 1. / 33 N-PEN-01 &
0.6447 / 33 N-HEX-01 0.6896 / 33 2-MET-01 0.6177 / &
33 2-MET-02 0.6989 / 33 CIS-2-01 0.6574 / 33 &
METHY-01 0.6864 / 33 BENZE-01 0.686 / 33 TOLUE-01 &
0.6728 / 33 O-XYL-01 0.6638 / 33 SULFO-01 0.6489 / &
34 N-PEN-01 0.6436 / 34 N-HEX-01 0.6909 / 34 &
2-MET-01 0.6167 / 34 2-MET-02 0.6963 / 34 CIS-2-01 &
0.6564 / 34 METHY-01 0.6895 / 34 BENZE-01 0.6888 / &
34 TOLUE-01 0.6756 / 34 O-XYL-01 0.6665 / 34 &
SULFO-01 0.6501 / 35 N-PEN-01 0.6428 / 35 N-HEX-01 &
0.6914 / 35 2-MET-01 0.6158 / 35 2-MET-02 0.6946 / &
35 CIS-2-01 0.6556 / 35 METHY-01 0.6915 / 35 &
BENZE-01 0.6904 / 35 TOLUE-01 0.6773 / 35 O-XYL-01 &
0.6682 / 35 SULFO-01 0.6507 / 36 N-PEN-01 0.6421 / &
36 N-HEX-01 0.6914 / 36 2-MET-01 0.6151 / 36 &
2-MET-02 0.6933 / 36 CIS-2-01 0.6549 / 36 METHY-01 &
0.6929 / 36 BENZE-01 0.6911 / 36 TOLUE-01 0.678 / &
36 O-XYL-01 0.669 / 36 SULFO-01 0.6507 / 37 &
N-PEN-01 0.6415 / 37 N-HEX-01 0.6911 / 37 2-MET-01 &
0.6145 / 37 2-MET-02 0.6923 / 37 CIS-2-01 0.6543 / &
37 METHY-01 0.6941 / 37 BENZE-01 0.6913 / 37 &
TOLUE-01 0.6781 / 37 O-XYL-01 0.6691 / 37 SULFO-01 &
0.6501 / 38 N-PEN-01 0.6409 / 38 N-HEX-01 0.6906 / &
38 2-MET-01 0.6139 / 38 2-MET-02 0.6915 / 38 &
CIS-2-01 0.6538 / 38 METHY-01 0.6953 / 38 BENZE-01 &

0.6913 / 38 TOLUE-01 0.6779 / 38 O-XYL-01 0.6689 / &
38 SULFO-01 0.6492 / 39 N-PEN-01 0.6404 / 39 &
N-HEX-01 0.69 / 39 2-MET-01 0.6134 / 39 2-MET-02 &
0.6907 / 39 CIS-2-01 0.6533 / 39 METHY-01 0.6968 / &
39 BENZE-01 0.6913 / 39 TOLUE-01 0.6774 / 39 &
O-XYL-01 0.6684 / 39 SULFO-01 0.6479 / 40 N-PEN-01 &
0.6399 / 40 N-HEX-01 0.6893 / 40 2-MET-01 0.6129 / &
40 2-MET-02 0.6901 / 40 CIS-2-01 0.6529 / 40 &
METHY-01 0.6985 / 40 BENZE-01 0.6915 / 40 TOLUE-01 &
0.6768 / 40 O-XYL-01 0.6677 / 40 SULFO-01 0.6461 / &
41 N-PEN-01 0.6395 / 41 N-HEX-01 0.6885 / 41 &
2-MET-01 0.6124 / 41 2-MET-02 0.6895 / 41 CIS-2-01 &
0.6525 / 41 METHY-01 0.7004 / 41 BENZE-01 0.692 / &
41 TOLUE-01 0.6761 / 41 O-XYL-01 0.6669 / 41 &
SULFO-01 0.6438 / 42 N-PEN-01 0.6391 / 42 N-HEX-01 &
0.6876 / 42 2-MET-01 0.612 / 42 2-MET-02 0.689 / &
42 CIS-2-01 0.6521 / 42 METHY-01 0.7026 / 42 &
BENZE-01 0.6932 / 42 TOLUE-01 0.6753 / 42 O-XYL-01 &
0.666 / 42 SULFO-01 0.6407 / 43 N-PEN-01 0.6388 / &
43 N-HEX-01 0.6865 / 43 2-MET-01 0.6117 / 43 &
2-MET-02 0.6885 / 43 CIS-2-01 0.6518 / 43 METHY-01 &
0.7048 / 43 BENZE-01 0.6952 / 43 TOLUE-01 0.6745 / &
43 O-XYL-01 0.6649 / 43 SULFO-01 0.636 / 44 &
N-PEN-01 0.6385 / 44 N-HEX-01 0.685 / 44 2-MET-01 &
0.6113 / 44 2-MET-02 0.6881 / 44 CIS-2-01 0.6515 / &
44 METHY-01 0.707 / 44 BENZE-01 0.6983 / 44 &
TOLUE-01 0.6736 / 44 O-XYL-01 0.6635 / 44 SULFO-01 &
0.629 / 45 N-PEN-01 0.6382 / 45 N-HEX-01 0.6828 / &
45 2-MET-01 0.611 / 45 2-MET-02 0.6878 / 45 &
CIS-2-01 0.6512 / 45 METHY-01 0.709 / 45 BENZE-01 &
0.7025 / 45 TOLUE-01 0.6727 / 45 O-XYL-01 0.6617 / &

45 SULFO-01 0.6178 / 46 N-PEN-01 0.6379 / 46 &
N-HEX-01 0.6793 / 46 2-MET-01 0.6107 / 46 2-MET-02 &
0.6874 / 46 CIS-2-01 0.651 / 46 METHY-01 0.7107 / &
46 BENZE-01 0.7075 / 46 TOLUE-01 0.6718 / 46 &
O-XYL-01 0.6593 / 46 SULFO-01 0.5988 / 47 N-PEN-01 &
0.6376 / 47 N-HEX-01 0.6731 / 47 2-MET-01 0.6104 / &
47 2-MET-02 0.6871 / 47 CIS-2-01 0.6507 / 47 &
METHY-01 0.712 / 47 BENZE-01 0.713 / 47 TOLUE-01 &
0.6715 / 47 O-XYL-01 0.6562 / 47 SULFO-01 0.5634 / &
48 N-PEN-01 0.6373 / 48 N-HEX-01 0.6604 / 48 &
2-MET-01 0.6101 / 48 2-MET-02 0.6868 / 48 CIS-2-01 &
0.6504 / 48 METHY-01 0.7129 / 48 BENZE-01 0.7181 / &
48 TOLUE-01 0.6725 / 48 O-XYL-01 0.6525 / 48 &
SULFO-01 0.486 / 49 N-PEN-01 0.637 / 49 N-HEX-01 &
0.6225 / 49 2-MET-01 0.6098 / 49 2-MET-02 0.6866 / &
49 CIS-2-01 0.6502 / 49 METHY-01 0.7135 / 49 &
BENZE-01 0.7223 / 49 TOLUE-01 0.6766 / 49 O-XYL-01 &
0.6484 / 49 SULFO-01 0.241 / 50 N-PEN-01 0.6367 / &
50 N-HEX-01 0.0001 / 50 2-MET-01 0.6094 / 50 &
2-MET-02 0.6864 / 50 CIS-2-01 0.6499 / 50 METHY-01 &
0.7137 / 50 BENZE-01 0.7256 / 50 TOLUE-01 0.6856 / &
50 O-XYL-01 0.6458 / 50 SULFO-01 0.0001 / 51 &
N-PEN-01 0.6363 / 51 N-HEX-01 0.8092 / 51 2-MET-01 &
0.609 / 51 2-MET-02 0.6861 / 51 CIS-2-01 0.6496 / &
51 METHY-01 0.7135 / 51 BENZE-01 0.7278 / 51 &
TOLUE-01 0.6991 / 51 O-XYL-01 0.6481 / 51 SULFO-01 &
1. / 52 N-PEN-01 0.6358 / 52 N-HEX-01 0.7568 / 52 &
2-MET-01 0.6085 / 52 2-MET-02 0.6859 / 52 CIS-2-01 &
0.6492 / 52 METHY-01 0.7129 / 52 BENZE-01 0.7292 / &
52 TOLUE-01 0.7139 / 52 O-XYL-01 0.6604 / 52 &
SULFO-01 1. / 53 N-PEN-01 0.6353 / 53 N-HEX-01 &

0.7414 / 53 2-MET-01 0.6078 / 53 2-MET-02 0.6856 / &
53 CIS-2-01 0.6487 / 53 METHY-01 0.7118 / 53 &
BENZE-01 0.7298 / 53 TOLUE-01 0.7266 / 53 O-XYL-01 &
0.6837 / 53 SULFO-01 1. / 54 N-PEN-01 0.6345 / 54 &
N-HEX-01 0.7344 / 54 2-MET-01 0.6069 / 54 2-MET-02 &
0.6853 / 54 CIS-2-01 0.648 / 54 METHY-01 0.7101 / &
54 BENZE-01 0.7297 / 54 TOLUE-01 0.7355 / 54 &
O-XYL-01 0.71 / 54 SULFO-01 1. / 55 N-PEN-01 0.6334 &
/ 55 N-HEX-01 0.7303 / 55 2-MET-01 0.6056 / 55 &
2-MET-02 0.6849 / 55 CIS-2-01 0.6472 / 55 METHY-01 &
0.7074 / 55 BENZE-01 0.729 / 55 TOLUE-01 0.7409 / &
55 O-XYL-01 0.73 / 55 SULFO-01 1. / 56 N-PEN-01 &
0.6318 / 56 N-HEX-01 0.7274 / 56 2-MET-01 0.6038 / &
56 2-MET-02 0.6842 / 56 CIS-2-01 0.6459 / 56 &
METHY-01 0.7031 / 56 BENZE-01 0.7275 / 56 TOLUE-01 &
0.7438 / 56 O-XYL-01 0.7414 / 56 SULFO-01 0.5339 / &
57 N-PEN-01 0.6295 / 57 N-HEX-01 0.7246 / 57 &
2-MET-01 0.6011 / 57 2-MET-02 0.6831 / 57 CIS-2-01 &
0.644 / 57 METHY-01 0.696 / 57 BENZE-01 0.7249 / &
57 TOLUE-01 0.7448 / 57 O-XYL-01 0.7466 / 57 &
SULFO-01 0.7064 / 58 N-PEN-01 0.6258 / 58 N-HEX-01 &
0.7213 / 58 2-MET-01 0.5967 / 58 2-MET-02 0.6812 / &
58 CIS-2-01 0.641 / 58 METHY-01 0.6823 / 58 &
BENZE-01 0.7204 / 58 TOLUE-01 0.7443 / 58 O-XYL-01 &
0.7482 / 58 SULFO-01 0.7384 / 59 N-PEN-01 0.6193 / &
59 N-HEX-01 0.7168 / 59 2-MET-01 0.589 / 59 &
2-MET-02 0.6776 / 59 CIS-2-01 0.6359 / 59 METHY-01 &
0.6468 / 59 BENZE-01 0.7127 / 59 TOLUE-01 0.7428 / &
59 O-XYL-01 0.7483 / 59 SULFO-01 0.7484 / 60 &
N-PEN-01 1. / 60 N-HEX-01 1. / 60 2-MET-01 1. / &
60 2-MET-02 1. / 60 CIS-2-01 1. / 60 METHY-01 1. / &

```
    60 BENZE-01 1. / 60 TOLUE-01 1. / 60 O-XYL-01 1. / &
    60 SULFO-01 1.
  L2-COMPS N-HEX-01 2-MET-01 2-MET-02 CIS-2-01 METHY-01 WATER &
    N-PEN-01
  L2-STAGES 2 59
  TRAY-REPORT PROPERTIES=VLLE
  TRAY-SIZE 1 2 3 SIEVE TRAY-SPACE=0.8 <meter> &
    MIN-DCAREA=0.12
  TRAY-SIZE 2 4 19 SIEVE TRAY-SPACE=0.8 <meter> &
    MIN-DCAREA=0.12
  TRAY-SIZE 3 20 32 SIEVE TRAY-SPACE=0.8 <meter> &
    MIN-DCAREA=0.12
  TRAY-SIZE 4 33 59 SIEVE TRAY-SPACE=0.8 <meter> &
    MIN-DCAREA=0.12
  TRAY-RATE 1 2 3 SIEVE TRAY-SPACE=0.8 <meter> &
    DIAM=5.3 <meter> EFF=0.6984 DC-CLEAR-SID=0.0381 <meter> &
    HOLE-DIAM=0.012 <meter> P-UPDATE=NO
  TRAY-RATE 2 4 19 SIEVE TRAY-SPACE=0.8 <meter> &
    DIAM=5.3 <meter> EFF=0.7038 DC-CLEAR-SID=0.0381 <meter> &
    HOLE-DIAM=0.012 <meter> P-UPDATE=NO
  TRAY-RATE 3 20 32 SIEVE TRAY-SPACE=0.8 <meter> &
    DIAM=5.3 <meter> EFF=0.6751 DC-CLEAR-SID=0.0381 <meter> &
    HOLE-DIAM=0.012 <meter> P-UPDATE=NO
  TRAY-RATE 4 33 59 SIEVE TRAY-SPACE=0.8 <meter> &
    DIAM=5.3 <meter> EFF=0.671 DC-CLEAR-SID=0.0381 <meter> &
    HOLE-DIAM=0.012 <meter> P-UPDATE=NO
  BLOCK-OPTION FREE-WATER=NO

BLOCK PUMP PUMP
  PARAM PRES=2.
```

```
OPTIMIZATION O-1
  DEFINE NPF MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=N-PEN-01
  DEFINE NHF MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=N-HEX-01
  DEFINE MB2F MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=2-MET-01
  DEFINE MP2F MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=2-MET-02
  DEFINE C2HF MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=CIS-2-01
  DEFINE MCPF MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=METHY-01
  DEFINE BZF MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=BENZE-01
  DEFINE TOLF MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=TOLUE-01
  DEFINE OXF MASS-FLOW STREAM=FEED SUBSTREAM=MIXED &
    COMPONENT=O-XYL-01
  DEFINE TMSF MASS-FLOW STREAM=SOLVENT SUBSTREAM=MIXED &
    COMPONENT=SULFO-01
  DEFINE NPN MASS-FLOW STREAM=NONARMTS SUBSTREAM=MIXED &
    COMPONENT=N-PEN-01
  DEFINE NHN MASS-FLOW STREAM=NONARMTS SUBSTREAM=MIXED &
    COMPONENT=N-HEX-01
  DEFINE MB2N MASS-FLOW STREAM=NONARMTS SUBSTREAM=MIXED &
    COMPONENT=2-MET-01
  DEFINE MP2N MASS-FLOW STREAM=NONARMTS SUBSTREAM=MIXED &
    COMPONENT=2-MET-02
  DEFINE C2HN MASS-FLOW STREAM=NONARMTS SUBSTREAM=MIXED &
    COMPONENT=CIS-2-01
```

```
    DEFINE MCPN MASS-FLOW STREAM=NONARMTS SUBSTREAM=MIXED &
      COMPONENT=METHY-01
    DEFINE BZB MASS-FLOW STREAM=BOTTOM SUBSTREAM=MIXED &
      COMPONENT=BENZE-01
    DEFINE TOLB MASS-FLOW STREAM=BOTTOM SUBSTREAM=MIXED &
      COMPONENT=TOLUE-01
    DEFINE OXB MASS-FLOW STREAM=BOTTOM SUBSTREAM=MIXED &
      COMPONENT=O-XYL-01
    DEFINE TMSB MASS-FLOW STREAM=BOTTOM SUBSTREAM=MIXED &
      COMPONENT=SULFO-01
F   P1=0.0059269*((NPF-NPN)/NPF)*((NPF-NPN)/NPF)
F   P2=0.006031045*((NHF-NHN)/NHF)*((NHF-NHN)/NHF)
F   I1=0.005926656*((MB2F-MB2N)/MB2F)*((MB2F-MB2N)/MB2F)
F   I2=0.005926471*((MP2F-MP2N)/MP2F)*((MP2F-MP2N)/MP2F)
F   O=0.018401121*((C2HF-C2HN)/C2HF)*((C2HF-C2HN)/C2HF)
F   N=53.10502772*((MCPF-MCPN)/MCPF)*((MCPF-MCPN)/MCPF)
F   A1=3.378518693*((BZF-BZB)/BZF)*((BZF-BZB)/BZF)
F   A2=0.00000044158103995 5857*((TOLF-TOLB)/TOLF)*((TOLF-TOLB)/TOLF)
F   A3=0*((OXF-OXB)/OXF)*((OXF-OXB)/OXF)
F   S=0*((TMSF-TMSB)/TMSF)*((TMSF-TMSB)/TMSF)
F   P=P1+P2
F   I=I1+I2
F   A=A1+A2+A3
F   OBJ=P+I+O+N+A+S
  MINIMIZE "OBJ"
  VARY BLOCK-VAR BLOCK=EDC VARIABLE=QN SENTENCE=COL-SPECS
  LIMITS "17" "23"
  VARY BLOCK-VAR BLOCK=EDC VARIABLE=MASS-D SENTENCE=COL-
SPECS
  LIMITS "1570" "1630"
  VARY BLOCK-VAR BLOCK=SPLIT SENTENCE=FRAC VARIABLE=FRAC &
```

```
    ID1=REFLUX
  LIMITS "0.8" "0.84"

CONV-OPTIONS
  PARAM TEAR-METHOD=BROYDEN TOL=0.0001
  WEGSTEIN MAXIT=500
  BROYDEN MAXIT=30
  NEWTON MAXIT=200 XTOL=0.01

TEAR
  TEAR REFLUX

STREAM-REPOR MOLEFLOW MASSFLOW MOLEFRAC MASSFRAC
;
```

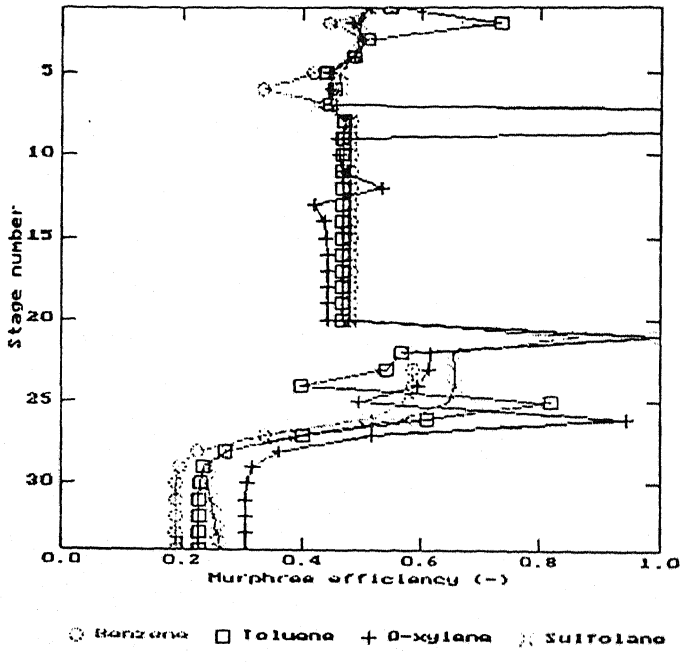



Figure C.1 Murphree efficiency plot for solvent recovery column.

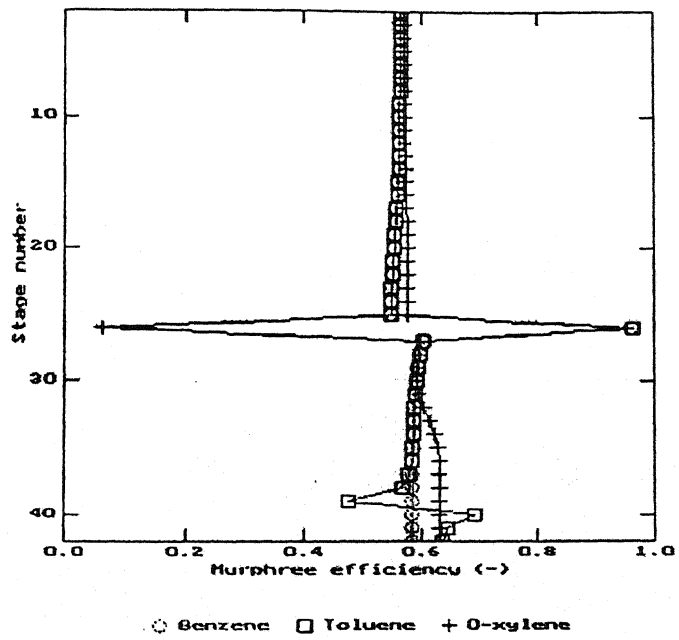



Figure C.2 Murphree efficiency plot for benzene column.

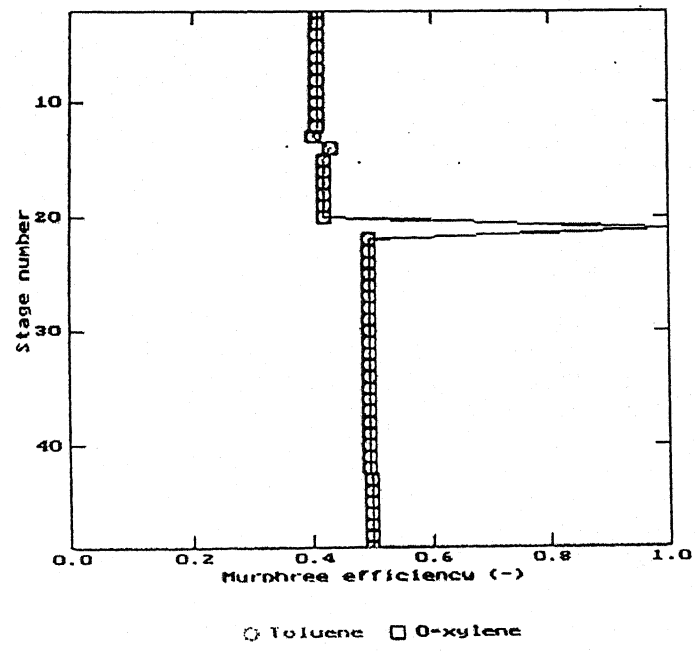



Figure C.3 Murphree efficiency plot for toluene column

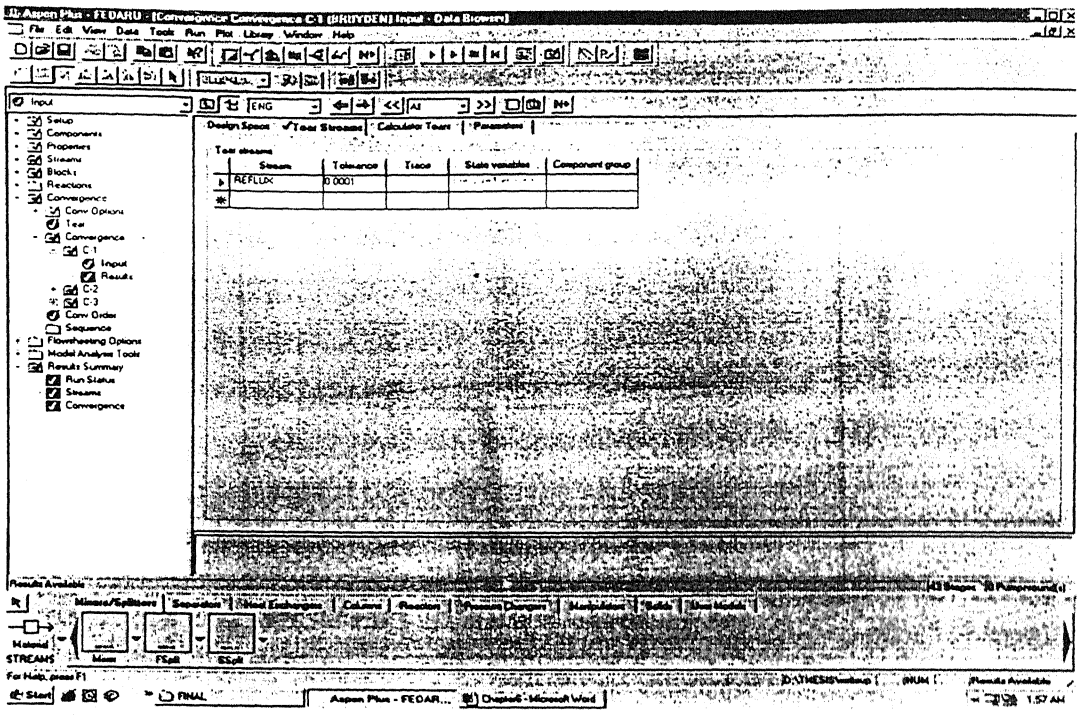


Figure C.4 User defined convergence block, C-1 input form for extractive distillation aromatic recovery unit

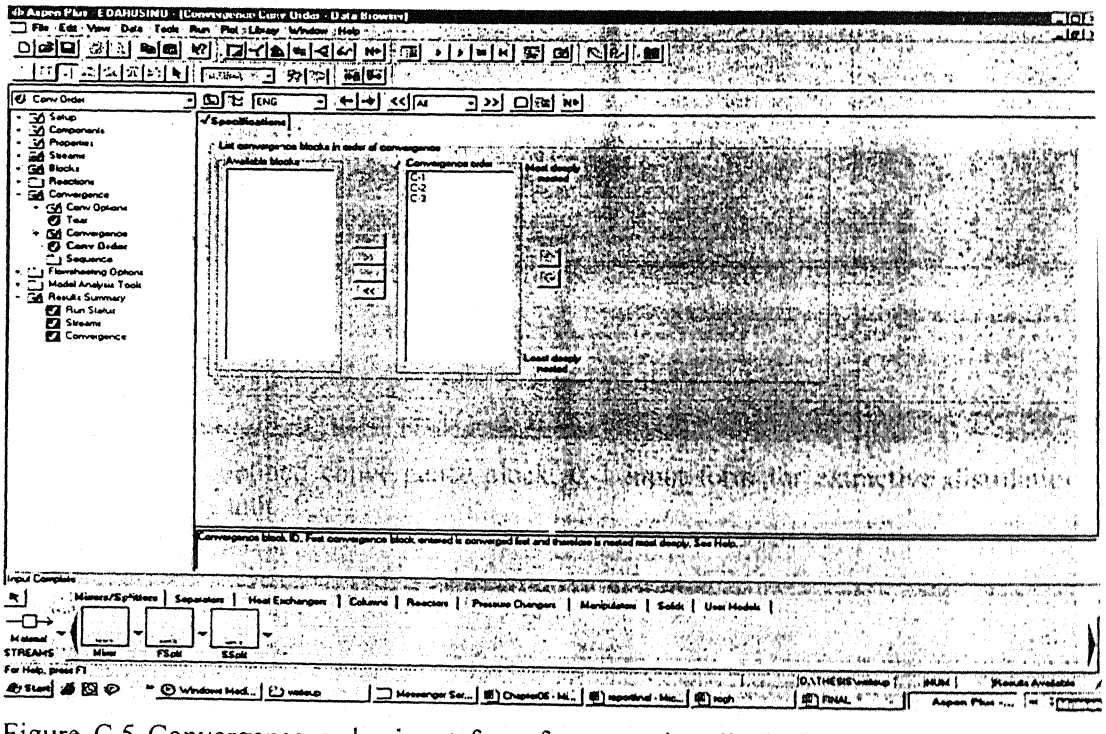


Figure C.5 Convergence order input form for extractive distillation aromatic recovery unit

# Volume, surface and UNIQUAC interaction parameters for imidazolium based ionic liquids via Polarizable Continuum Model

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(Fluid Phase Equilibria 234 (2005) 64)

## Abstract

Ionic liquids (ILs) have shown great potential as solvent/media for reactions and separations. However, the physico-chemical characteristics of ILs are scarce and the limitless different combinations of cations and anions further complicate the matter. The ternary tie line data along with the binodal curve gives a fair indication regarding the feasibility of the ILs as solvents. Most of the ternary (with ILs) liquid–liquid equilibrium data available in literature has been correlated through the NRTL model as $r$ and $q$ are not available. The absence of the volume and surface parameters poses a hindrance in calculation of the binary interaction parameters for UNIQUAC and UNIFAC models. A novel method has been developed for deriving these volume and surface parameters from the Polarizable Continuum Model (PCM). PCM is widely used for studying solvation effects. Here, the solute is represented by a charge distribution in a molecular shaped cavity embedded in an infinite polarizable dielectric medium. GEnerating POLyhedra (GEPOL), which is based on the concept of solvent excluding surface, is used for calculating this cavity. This novel approach for volume and surface parameters has been verified initially for 71 compounds belonging to several homologous series (paraffins, isoparaffins, olefins, naphthenes, aromatics, alkynes, alcohols, ketones, aldehydes, acids, esters and amines) and 24 solvents. The predicted values of $r$ and $q$ for alcohols, ethers and oxygen containing systems showed significant deviations (2.5–20% for $r$ and 5–25% for $q$ ) from the literature values. The values of $r$ and $q$ obtained by PCM method have been applied to 17 ternary systems and 1 quaternary system belonging to these deviant components. The PCM method gives a significantly better fit (average of 60% improvement in rmsd) for all the systems studied. This approach has been used to estimate the structural parameters for 25 dialkylimidazolium based ILs. Subsequently, these values have been used to estimate the UNIQUAC interaction parameters for seven IL based ternary systems, giving a 40% improvement in rmsd over NRTL.

*Keywords:*Polarizable Continuum Model; Volume and surface parameters; Solute cavity; Gaussian 98; Imidazolium based ionic liquids

# Improved Binary Parameters using GA for Multi-Component Aromatic Extraction
## UNIQUAC Model without and with Closure Equation/s

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(Journal of Chemical Thermodynamics, Submitted)

**Abstract**

Application of *Genetic Algorithm* (GA) which leads to globally optimal binary interaction parameters from multi-component liquid-liquid equilibrium data has been recently demonstrated for some ternary, quaternary and quinary systems [M. K. Singh, T. Banerjee, A. Khanna, Computers & Chemical Eng. 29 (2005) 1712-1719]. The binary interaction parameters are related to each other through the *closure equation/s* [S. A. Ahmad, A. Khanna, Korean J. Chem. Eng. 20 (2003) 736-744]. In this work, the binary interaction parameters based on UNIQUAC activity coefficient model have been estimated using GA without and with closure equation/s for 65 multicomponent aromatic extraction systems; 53 ternary, 9 quaternary, and 3 quinary systems. Parameters that satisfy the closure equation/s exhibit better root mean square deviations than those that do not satisfy the closure equations/s. Average root mean square deviation (rmsd) value without implementation of closure equation/s is approximately 20 percent better than literature as compared to 30 percent better with implementation of closure equation/s.

*Keywords:* Aromatic extraction; Liquid-liquid equilibria; UNIQUAC; Binary interaction parameters; Closure equation/s; GA

# Improved Binary Parameters using GA for Multi-Component Aromatic Extraction
# NRTL Model without and with Closure Equation/s

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(Fluid Phase Equlilibria, Submitted)

**Abstract**

Application of *Genetic Algorithm* (GA) which leads to globally optimal binary interaction parameters from multi-component liquid-liquid equilibrium data has been recently demonstrated for some ternary, quaternary and quinary systems [M. K. Singh, T. Banerjee, A. Khanna, Computers & Chemical Eng. 29 (2005) 1712-1719]. The binary interaction parameters are related to each other through the *closure equation/s* [S. A. Ahmad, A. Khanna, Korean J. Chem. Eng. 20 (2003) 736-744]. In this work, the binary interaction parameters based on NRTL activity coefficient model have been estimated using GA without and with closure equation/s for 65 multicomponent aromatic extraction systems; 53 ternary, 9 quaternary, and 3 quinary systems. Parameters that satisfy the closure equation/s exhibit better root mean square deviations than those that do not satisfy the closure equations/s. Average root mean square deviation (rmsd) value without implementation of closure equation/s is approximately 36 percent better than literature as compared to 43 percent better with implementation of closure equation/s.

*Keywords:* Aromatic extraction; Liquid-liquid equilibria; NRTL; Binary interaction parameters; Closure equation/s; GA

*This is not the end.....*

*This is the beginning of another end*